SUMMARY.

THE PREPARATION AND PROPERTIES OF SOME HYDRAZINIUM AND KETAZINIUM COMPOUNDS.

Previous work (Pugh and co-workers) had shown the existence of a new type of salt. It had, prior to this, seemed unlikely that hydrazine salts and ketones would condense together under the strongly acid conditions prevailing, because the formation of ketazines and hydrazones is generally held to take place in neutral or alkaline conditions. Subsequently similar salts were prepared from aldehydes.

All these salts were prepared from a limited number of ketones and aldehydes, and it seemed necessary to extend the work to aldehydes and ketones in general to show that the salt forming properties were possessed by all types of aldehydes and ketones. This was done successfully, salts being prepared from both aromatic and aliphatic aldehydes and ketones, with both simple and complex anions. The difficulties were mainly those of preparative techniques and analysis.

In addition to the preparation of the compounds and investigation of some of their properties, a new analytical method for estimating halogen in halegenoplatinates was developed.

When salts could not be prepared it was usually because the relatively less soluble hydrazinium salt precipitated first. In some cases, especially with the aliphatic ketones, the simple salts could not be prepared because of the instability of the ketazinium or hydrazonium ions concerned. In other cases viscous oils were formed,

an important factor no doubt being favourable ionic sizes for building up the crystal pattern.

Pugh and his co-workers had also prepared a number of hitherto unrecorded hydrazinium salts. These salts were similar to those previously reported and bore no relationship to the ketazinium salts.

Two points emerged from this work. One was the preparation of hydrazinium hexachloro - and hexabromoaluminates; which indicated six co-ordinations of aluminium by chlorine and bromine and seemed unlikely. The other was that a pentafluoroaluminate was prepared in crystalline form, and this was at variance with earlier reports of this compound. The work was extended to the other group IIIB compounds gallium and indium.

The complex hydrazinium chlorides, bromides and iodides of gallium and indium could not be prepared. In all the preparations attempted the relatively less soluble hydrazinium halides precipitated from solution.

The crystal structure of the hydrazinium hexachloroaluminate prepared by Pugh and his co-workers has since been examined by means of X-Ray crystallography and it has been shown that the compound was not the complex described. The hexa-halides therefore do not appear to exist, the compounds obtained being mixed, hydrated, salts which have precipitated together from solution.

The hydrazinium fluorogallates and fluoroindates were prepared

by seven different procedures. A crystalline, hydrated, pentafluorogallate was obtained, and amorphous, anhydrous, di-hydrazinium hexafluoro-gallates and indates were prepared. Also prepared were a number of hexafluoro-gallates and indates with extra hydrogen fluoride present. These compounds could be grouped into three categories: compounds with two or three molecules of hydrogen fluoride extra, compounds with nine to eleven molecules of hydrogen fluoride extra, and compounds with fourteen molecules of hydrogen fluoride extra.

The crystal structure of the pentafluorogallate could not be determined as the crystals obtained were too small to be characterised.

The hexafluorides were investigated by means of conductimetric and high-frequency titrations and by conductance measurements. All that resulted from these experiments was the fact that a complex was present and that three of the fluorine atoms behaved differently from the other three.

The compound with fourteen extra hydrogen fluoride molecules present was examined by expelling hydrogen fluoride from the compound by heating. Loss of weight at different temperatures, and rate of loss of weight at fixed temperature and pressure curves were determined. Samples taken at various stages of the heating were analysed to determine the extent of decomposition. As a result of these experiments it was shown that three of the hydrogen fluoride molecules present could be lost comparatively easily and were most likely adsorbed. The other eleven molecules could only be removed by decomposing the

compound. They were therefore more likely to be interstitially held, and to be part of a definite complex compound. To see whether the ability to hold extra hydrogen fluoride was a property of the complex only, attempts were made to prepare hydrazine dihydrofluoride and gallium trifluoride with extra hydrogen fluoride present. A large number of preparations were undertaken, using different techniques. In no case was a hydrazinium compound found with more than two fluorine atoms, and in only one case was a gallium compound with more than three fluorine atoms isolated. This compound was GaF_3 $3H_2$ O. HF; the extra hydrogen fluoride being lost very easily on keeping the compound under vacuum.

THE PREPARATION AND PROPERTIES

of some

HYDRAZINIUM and KETAZINIUM COMPOUNDS.

DISSERTATION

SUBMITTED TO THE UNIVERSITY OF CAPE TOWN

FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

BY

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March, 1957.

ACKNOWLEDGEMENTS.

I would like to express my debt of gratitude to the late Professor W. Pugh, F.R.S.S.Af., whose guidance and kindness in sharing of his experience were of considerable help during the early stages of this thesis.

My thanks also to Dr. A.H. Spong and to Dr. R. Arnold, who supervised the latter part of this work, for their interest and unstinted help; to Mr. W.C. Lewis and Mr. D. O'Neill for their assistance in building special apparatus; to Professor W. Schaffer for X-ray examinations; to the National Chemical Research Laboratory, Pretoria, for Infra-red analyses and to the National Physical Laboratory, Pretoria, for Raman analyses.

Finally I would like to express my thanks to the Administrators of the Fourquade Bequest and the Staff Research Fund for grants for chemicals and apparatus.

C O N T E N T S.

CHAPTER I.

INTRODUCTION.

Although the chemistry of hydrazine has been studied for almost three quarters of a century, for many years it was considered a speciality chemical available only in aqueous solution and in the form of a few of its common salts. During World War II its interesting fuel properties were discovered, and since then with the availability of concentrated hydrazine solutions it has been subjected to extensive research.

When dissolved in water hydrazine yields a solution with basic properties. The dissociation constants at 25°C have been calculated[1] and the following values reported:

$$K_I = \frac{[N_2H_5^+]\,[OH']}{[N_2H_4]} = 8.5 \times 10^{-7}$$

$$K_{II} = \frac{[N_2H_6^{++}]\,[OH']}{[N_2H_5^+]} = 8.9 \times 10^{-16}$$

The value for the second constant is so small that it has been generally accepted that diacid salts of hydrazine do not exist in aqueous solution, the $N_2H_6^{++}$ ion reacting completely with the solvent water according to the equation:

$$N_2H_6^{++} + H_2O \rightarrow N_2H_5^+ + H_3O^+$$

Since hydrazine is primarily a mono-acid base it resembles ammonia and the amines rather than the organic diamines as is evident from a comparison of the respective dissociation constants and an examination of the heats of neutralisation of the respective bases with acids in

aqueous solution.[2,3]

Hydrazine, however, forms not only mono- and di-acid salts of the type N_2H_5A, $N_2H_6A_2$ where HA represents a monobasic acid, but also compounds of the types $(N_2H_5)_2B$, N_2H_6B and $N_2H_6.(HB)_2$ where H_2B represents a dibasic acid. In addition there are also known several series of so called double salts prepared by bringing together in aqueous solution the corresponding metallic and hydrazine salts in the proper molecular proportions. Druce[4] had reported a substance formulated as $N_2H_4.H_2SnCl_6$ ($N_2H_6SnCl_6$) this being the only chlorostannate mentioned in the literature prior to 1950. This formulation though in harmony with that of the chlorostannates of ethylenediamine and phenylenediamine also prepared by Druce, seemed unlikely as the compound had been prepared from stannic chloride and hydrazine monohydrochloride* which would be expected to yield dihydrazinium chlorostannate $(N_2H_5)_2SnCl_6$.

Pugh and Stephen[5] repeated this work using stannic chloride and varying amounts of hydrazine mono- and dihydrochloride in the presence of water, but the only compound they were able to isolate was the dihydrazinium chlorostannate. Under anhydrous conditions hydrazine dihydrochloride failed to react, while hydrazine monohydrochloride reacted vigorously giving the dihydrazinium chlorostannate.

Presumed salts of ketazine and hydrazones.

The chlorostannate separated from water in the anhydrous condition

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* Although a consistent rational system of naming hydrazine salts would be desirable, usage has conventionalised certain inconsistencies. Because hydrazine compounds have been widely used by organic chemists the system of nomenclature used by these chemists is employed in this thesis.

but when obtained from aqueous acetone or aqueous butanone mixtures separated with what appeared to be ketone of crystallisation. Subsequent work[6], however, indicated that the compounds were chlorostannates of dimethyl ketazine and butanone hydrazone respectively.

Pugh[7,8] extended this work and prepared the bromostannates and bromostannites of hydrazine, dimethyl ketazine, and pentan-3-one hydrazone; and also the halogeno- antimonites, and -bismuthites of dimethyl ketazine, butan-3-one hydrazone, pentan-3-one hydrazone, and heptan-3-one hydrazone. Attempts to make similar compounds from hydrazine condensed with ethyl-methyl ketone or di-n-propyl ketone were unsuccessful yielding viscous solutions that could not be induced to crystallise even after several months at -10°C.

Shoesmith and Slater[9] had previously reported a chlorostannate of anisaldazine, and Sohn[10] paralleling the work outlined above had prepared a number of halogeno-antimonites, -bismuthites, and -stannates of various aromatic aldazines. Sohn had also prepared a number of simple aldazinium salts from aromatic aldehydes. Attempts to prepare compounds from aliphatic aldehydes, however, had proved unsuccessful.

At this stage therefore some complex salts from the azines or hydrazones of a number of aliphatic ketones (but not aldehydes) and a number of simple and complex salts from some aromatic aldehydes (but not ketones) had been prepared. Part of the work presented in this thesis was undertaken to survey the salt forming properties in general; to see whether aromatic ketazines or aliphatic aldazines would form salts and also whether simple salts could be obtained from ketazines.

The Halegeno-gallates and halegeno-indates of hydrazine.

The remainder of this thesis deals with the preparation of some hydrazinium halides of gallium and indium.

Complex fluorides of the hydrazinium ion described in the literature include the fluoro-silicate and titanate[11], -aluminate[12], -borate[13], -beryllate[14], and -germanate[15]. Pugh[16] recently prepared the hydrazinium salts of complex fluoro-acids of tin, antimony and bismuth.

The complex halides constitute the most abundant class of complexes formed by the Group III b elements; the distribution however is curious. According to Sidgwick[67], gallium forms only complex fluorides; indium only chlorides and bromides; and thallium complex chlorides, bromides and iodides. Einecke[68] on the other hand reports a complex chlorogallate NH_4GaCl_4.

The complex indium halides are all chlorides or bromides. Meyer[48] prepared the soluble salts $K_3(InCl_6)1.5H_2O$ and $(NH_4)_2\ (InCl_5(OH)_2)$. Ekeley and Potraz[49] made a series of complex indium chlorides and bromides of alkyl amines; the types of salts varied from $MInX_4$ to $M_4\ In\ X_7$; the (apparent) covalency of the metal in the anion being on the whole greater the fewer alkyl groups were attached to the nitrogen.

The first complex fluorogallates were made by Hannebohn and Klemm[50] and were further examined by Pugh[51,52]. They were made by mixing the components in dilute hydrofluoric acid solution, and are all of the type M_3GaF_6. Their hydration, however, is very peculiar. When recrystallised from water the lithium, sodium and ammonium salts have no water of crystallisation, the potassium salt has one molecule of water of

of crystallisation and the rubidium and caesium salts two molecules, the hydrated forms all lose their water on being heated at 230°C.

Later Pugh[52] prepared a series of salts of divalent metals, especially of the type $M^{2+}(GaF_5)$, $7H_2O$ or $M^{2+}(GaF_5(OH)_2)$, $6H_2O$ where $M^{2+} = Mn^{2+}$, Co^{2+}, Ni, Cu^{2+}, Zn and Cd. These are all readily soluble in water.

Also reported are a number of solid amines with a large number of NH_3 molecules from the trichlorides, tribromides and triiodes of gallium[53] and indium[54,55] and with a smaller number from the trifluorides[56] where the highest are GaF_3, $3NH_3$ and InF_3, $3NH_3$.

Einecke[68] also reports the existence of $[(H_2O)_3\ Ga\ (NH_3)_3]\ [GaF_6]$, $(NH_4)_2\ [GaF_5]$ and of $NH_4\ (GaF_4)$.

Weinland et al[12] had reported a penta-fluoro-aluminate of hydrazine of somewhat variable composition, described as a non-crystalline white powder. Hotz and Pugh[17], however, obtained it as an anhydrous crystalline product whose optical properties have been examined. They also report the existence of hydrazinium hexachloro- and hexabromo-aluminates. This was surprising in that it seemed to indicate 6 - co -ordination of aluminium by chloride and bromine which is both unknown and unexpected.

In view of this interesting result it was decided to extend this work to the Group III b elements. Only gallium and indium were used, as thallium behaves differently from gallium and indium (and hence from aluminium) in its properties.

CHAPTER II

SOME SALTS OF ALDAZINES AND KETAZINES.

(1) Halegeno - platinates of the aldazines and ketazines.

Prior to the work of Pugh and his co-workers (see Introduction, pp. 2,3) it had seemed unlikely that hydrazine salts and ketones would condense together under the strongly acid conditions prevailing, because the formation of ketazines and hydrazones was generally held to take place under neutral or alkaline conditions.

The stability of dimethyl ketazine in water has been investigated by Gilbert[70] who states that it is soluble in water, yielding an alkaline solution, and that if the hydroxyl ions are removed by acids more are produced. In strong mineral acids, it is completely hydrolysed to hydrazinium ions and acetone. Hydrolysis is, however, reversible involving acetone hydrazonium ion as well as hydrazinium ion. While hydrolysis is promoted by acids, it is repressed by addition of acetone and Gilbert reaches the conclusion that, in the presence of acetone, dimethyl ketazine does not function as a base. The hydrolysis and formation of dimethyl ketazine, according to Gilbert, proceeds according to the following equations:-

$$Me_2\,C{:}\,N.\,N{:}\,C\,Me_2 + H^+ + H_2O \rightleftharpoons [Me_2\,C{:}\,N.NH_3]^+ + Me_2\,CO$$

$$[Me_2\,C{:}\,N.NH_3]^+ + H_2O = [N_2H_5]^+ + Me_2\,CO$$

Conant and Bartlett[71], on the other hand, suggest that the formation of semi-carbazones and related substance proceeds by reaction between neutral molecules of semi-carbazide and ketones. This reaction was

shown to be catalysed, not only by hydrogen ions, but also by acid molecules in the Bronsted sense. They showed too, that these semi-carbazones, like the ketazines, are progressively hydrolysed at increasing acidities.

Since all these observations were made in very dilute solutions, the conclusions to be drawn from them are not necessary valid for the concentrated solutions used by the above workers. It was particularly noted that some of the salts separated from strongly acid solutions which indicated that dimethyl ketazinium ions and ketone hydrazinium ions must exist in considerable concentration in strongly acid solutions, without the need of excess ketone to repress hydrolysis.

Pugh[8] therefore suggested a mechanism that for these salts condensation proceeds between hydrazinium ions and ketone as suggested by Gilbert; the process being subject to general acid catalysis as suggested by Conant and Bartlett. He put forward also reasons for their being regarded as salts, viz. appearance, behaviour to acids and alkalis, and the fact that acetone solutions of these substances are excellent conductors of electricity.

All these salts were prepared from a limited number of ketones and aldehydes and it seemed necessary to extend the work to show that all types of aldehydes and ketones possess salt forming properties.

The first requirement was a stable anion. The hexa - halides of platinum are well known, being used especially for the characterisation of amines. It seemed most likely that chloro- or bromo-platinic acid would yield salts with aldazines and ketazines and that these salts

would be stable enough to be isolated. This supposition proved correct although decomposition of the anion due to the presence of hydrazine caused some difficulties. This reduction, however, lead to the development of a new method of estimating halogens in halegeno-platinates (See "Analytical Methods").

The first compounds attempted were those using the aliphatic ketones that had been used by the earlier workers. Then other aliphatic ketones and some aromatic ketones were employed, these were followed by aromatic and aliphatic aldehydes; and finally the preparation of salts of azines prepared by condensing various combinations of aliphatic/aromatic aldehyde with hydrazine and aliphatic/aromatic ketone was attempted.

Although a number of salts could not be prepared, sufficient compounds were obtained to show that the salt forming properties were general and were not restricted to any particular type of aldehyde or ketone.

Salts were obtained from (See Table I)

- Acetone Ketazine
- di-Ethyl ketazine
- Benzalazine
- Acetophenoneazine
- Acetaldazine *
- Propionaldazine *
- "Mixed" azines from
  - Acetophenone and Benzaldehyde
  - Acetone and acetaldehyde

* Partially polymerised products were obtained.

No salts were obtained from

- Ethyl methyl ketazine
- di-n-Propyl ketazine
- Methyl-n-propyl ketazine
- Methyl-iso propyl ketazine
- Methyl-di-iso-propyl ketazine
- Benzophenoneazine
- n-Butyraldazine
- "Mixed" azines from
  - Acetone and benzaldehyde
  - Acetophenone and acetaldehyde
  - Acetaldehyde and benzaldehyde
  - Acetone and acetophenone.

TABLE .I

Halogeno-platinates of some azines and hydrazones. $(R:N.N:R')_2H_2MX_6$

R	R'	X	Melting Point °C	Appearance		Analysis N_2H_4	Pt.	X	C	H
$(CH_3)_2C$	$(CH_3)_2C$	Br	82-84	Red crystalline birefracting	Found:	6.9	22.9	54.5		
					Reqd.:	7.1	21.7	53.3		
$(CH_3)_2C$	$(CH_3)_2C$	Cl	157-158 decomposes	Orange crystalline birefracting	Found:	10.5	31.4	33.6*		
					Reqd.:	10.1	32.2	35.1		
$(CH_3CH_2)_2C$	H	Br	Blackens 135 decomp. at 170	Dark red Amorphous	Found:	6.3	21.7	56 *		
					Reqd.:	7.3	22.3	54.7		
$(CH_3CH_2)_2C$	H	Cl	Darkens 120 melts 187-188	Yellow-orange Amorphous	Found:	10.4	34.5	34.8*		
					Reqd.:	10.5	32.1	35.1		
C_6H_5CH	C_6H_5CH	Br	188-189	Orange Amorphous	Found:	5.9	18.7	44.1		
					Reqd.:	5.9	17.9	43.8		
CMePh	CMePh	Br	190-191	Red crystalline birefracting with straight extinction	Found:	5.6	17.1	42.5		
					Reqd.:	5.7	17.3	42.5		
C_6H_5CH	CMePh	Br	214-216	Red crystalline birefracting with straight extinction	Found:	5.0	15.1	37.4		
					Reqd.:	5.0	15.2	37.4		
CH_3CH	CH_3CH	Br	106-107	Orange Amorphous	Found:	6.0	18.5	45.4	18.1	3.5**
					Reqd.:	6.0	18.3	45.0	14.6	3.6
CH_3CH_2CH	CH_3CH_2CH	Br	78-79	Orange Amorphous	Found:	6.0	18.7	45	21.4	3.7**
					Reqd.:	6.3	19.2	47.3	21.3	3.7
$(CH_3)_2C$	CH_3CH	Br	94-96	Orange Amorphous	Found:	6.3	18.8	41.8		
					Reqd.:	6.2	18.9	46.4		

* On dissolving in water reduction occurred.

** Polymerised product.

(2) Simple salts of ketazines.

Some simple aromatic aldazinium salts (i.e. salts with simple halide or sulphate anion) had been prepared but no such ketazine salts had been isolated.

As the aldazinium salts had all been aromatic, initially aromatic ketones were used.

The simplest aromatic ketone acetophenone was employed, and the substituted acetophenones were tried to see whether the substituent group had any effect on the formation of salts. One would expect electron repelling groups in the ortho and para positions to increase the basicity while electron attracting groups would have the opposite effect.

Benzophenone was then used and this was followed by a series of preparations using azines from aliphatic ketones. Finally, attempts were made to prepare salts from azines made by condensing one molecule of hydrazine with an aliphatic and an aromatic ketone; and from an azine prepared from an alicyclic ketone.

In order to eliminate hydrolysis as far as possible, a vacuum train was built for some of these preparations (see Experimental, p. 79). The only compounds that could be induced to give salts, however, were the aromatic ketones, acetophenone and benzophenone. When salts could not be prepared it was usually because the relatively less soluble hydrazinium salt precipitated first. In some cases especially with the aliphatic ketones, the simple salts could not be prepared because of the instability of the ketazinium or hydrazonium ions contained.

In other cases viscous oils were formed, an important factor, no doubt, is favourable ionic sizes for building up the crystal pattern.

Salts were obtained from: (See Table II)
- Acetophenone azine
- Benzophenone azine

No salts obtained from:
- m-Nitro-acetophenone azine
- o-Hydroxy-acetophenone azine
- p-Methoxy-acetophenone azine
- di-Methyl ketazine *
- Ethyl-methyl ketazine *
- di-Ethyl ketazine
- n-di-Propyl ketazine
- n-di-Butyl ketazine
- Mixed acetone-acetophenone azine
- Cyclohexanone azine

* Impure products were obtained with these compounds.

TABLE II.

Compounds of the general type (R:N.N:R)HX

R	X	M.Pt.	Formula	Found (%)		Required (%)		Method
				N_2H_4	X †	N_2H_4	X †	
CMePh	Cl	132-134	$C_{16}H_{17}N_2Cl$	11.8	13.4	11.7	13.0	a
CMePh	HSO_4	125-126	$C_{16}H_{17}N_2HSO_4$	9.8	29.4	9.6	28.8	b
CPh_2	Cl	166-168	$C_{26}H_{21}N_2Cl$	8.1	9.0	8.1	9.2	a

† Here X = halogen or SO_4 not HSO_4.

Method a) Hydrogen chloride was passed through a solution of the azine in ether.

b) An equivalent quantity of sulphuric acid (98%) in ether solution was added to the azine in ether.

(3) Discussion

This survey resulted in the preparation of halides, sulphates and halogeno-platinates of a variety of azines. The following points emerge:

(i) Aromatic ketazines yielded halides, sulphates and complex salts.

(ii) Aliphatic ketazines gave salts less readily. No simple salts were obtained, although in some cases oily products were obtained, at -50°C or below, which showed variable composition indicating varying degrees of polymerisation. Dimethyl ketazine yielded complex salts but its homologues, under comparable conditions, formed salts of the corresponding hydrazones instead; thereby confirming earlier work[6,7,8].

(iii) "Mixed" azines containing 1 mol. each of ketone and aldehyde condensed per mol. of hydrazine also gave salts.

The view that these compounds were salts was based on the following properties: (a) generally they were crystalline and salt-like. (b) In their behaviour towards water, acids and alkalis they resembled the corresponding ammonium and potassium salts. (c) They dissolved (in most cases) fairly readily in dilute acids, the solutions containing hydrazine salts and free ketone. They are insoluble in cyclohexane, ether and xylene, but dissolve in ketones. (d) The

complex platinates were all red in colour and behaved similarly to other halogeno platinates in that transmission of light by their solutions did not obey Beer's Law. The transmission of light by solutions of the water soluble bromoplatinates was investigated, using a Leitz Colorimeter (Model 671).

Light absorptions were difficult to determine; as solutions of the salts were very unstable, decomposition to colloidal platinum occurring in almost every case.

The best results were obtained with acetone ketazine (see Table III. Here the error was 14.75%. (Accuracy of the method approx. 7%).

TABLE III.

Concentration C mgm./100 c.c.	Depth t	t C	Error	% Error
27.0	29.2	788	-	-
13.5	49.97	674	114	14.75
6.75	unable to effect balance	-	-	-

(e) Acetone solutions of these salts were good conductors of electricity. (f) The salts showed the expected gradation in melting points, the melting point rising with increasing complexity of the base for the same anion. It is true that they have low melting points (< 220 C) and decompose when heated above their melting points, but these properties are shared also by the simple hydrazine salts.

The inability to obtain some of the salts might be explained to some extent by the lack of favourable ionic sizes for building up the

crystal lattice. Another reason might be their solubilities, concentration of the solution yielding the relatively less soluble halides of hydrazine as the first product. Similar results have been noted by earlier workers who prepared "double halides" of hydrazine[4,35,39,40,41,42,43].

The fact that the higher aliphatic ketones gave hydrazonium instead of ketazinium salts, might have been due to lack of free rotation of the azine in the molecule, or again to the ionic sizes required to build up a crystal. Models of the various azines were made using "Catalin" models. Free rotation was possible, i.e. ionic sizes appear to be the limiting factor.

In two cases co-ordination products appear to have formed. The early attempts to produce the salt from di-ethyl ketone yielded $(N_2H_4)_2$ Pt Cl_4 and attempts to make the salt from ethyl methyl ketone gave a compound having the apparent formulation $[Pt\ Br\ (H_2O)_2(N_2H_4)_3]Pt\ Br_6$.

Platinum compounds containing co-ordinated hydrazine are somewhat limited in number because of the reducing nature of hydrazine. In most cases recorded, hydrazine has acted as a bidentate co-ordinating molecule. Specific evidence that it can occupy only one co-ordination position is offered by a number of Russian investigators. Amongst the compounds reported are $[Pt(N_2H_4)_4]Cl_2$ and $[Pt(NH_3)_2(N_2H_4)_2]Cl_2$[44].

In aqueous solution the first of these compounds decomposed, especially on the addition of alkali with effervescence and liberation of platinum. An aqueous solution of the latter on being treated with hydrochloric acid gave $[Pt(NH_3)_2(N_2H_4)_2]Cl_2.2HCl$; this with

potassium chloroplatinite yielded $[Pt(NH_3)_2(N_2H_4)_2]_2(PtCl_4)_3$. On boiling with dilute hydrochloric acid this last compound decomposed to form hydrazine hydrochloride and platinous cis-dichloro diamine.

The above compounds, however, are platinous compounds, whereas the ones obtained during the course of this work are platinic.

Co-ordination could explain the slow titrations when hydrazine was determined in these compounds by Andrews' method. The possibility exists that

$$(PtCl_6)^{2-} + 2N_2H_5^+ \rightarrow PtCl_4(N_2H_4)_2 + 2HCl$$

or $$(PtBr_6)^{2-} + 2N_2H_5^+ \rightarrow PtBr_4(N_2H_4)_2 + 2HBr,$$

the hydrazine molecule co-ordinating with one of the NH_2 groups replacing a halogen which is of comparable size. Water molecules could also replace the halogen.

If the hydrazine is co-ordinated it will not react easily with the iodate solution. On standing some of the molecules are dislodged by collisions and are then available for reaction. Increasing the temperature (i.e. the number of collisions) caused the titration to proceed far more rapidly (2-3 minutes instead of $\pm$ 30 hours). Acetaldazine and propionaldazine also gave slow hydrazine titrations, here, however, polymerisation appeared to have taken place. In these polymerised compounds half of the hydrazine reacted immediately, the other half very slowly.

Sohn[10] had also obtained similar results with acetaldazine.

She, however, had 5 aldehyde molecules (mol. wt. of base 455 wt. units) more than expected, the compound discussed above had 3 extra molecules (mol. wt. of base 351 wt. units). Her compound gave no immediate hydrazine titration whereas the bromoplatinate gave one mol. instantly. Possibly the latter compound is polymerised to a lesser extent.

Infra-red analyses were done on both the acetaldazine (A) and propionaldazine (P) bromoplantinates by the N.C.R.L., Pretoria, no facilities being available in these laboratories. The spectra were run off in the solid state, in pressed KBr discs, from 2 - 15μ. The chief bands, none of which were well defined, (with tentative assignments) were as follows:-

A	P	
2.93	2.43	N-H stretching; -OH groups
3.40	3.40	C-H stretching
3.84	3.88	?
	4.03	?
6.15	6.15	-C=N stretching; or -C=C-
6.48	6.56	-N-H-
6.90	6.87	C-H deformation; active H, vinyl group
7.05		?
7.21	7.21	CH_3 group
7.72		-COH, $-OCH_3$.

Absence of strong absorbtion at about 5.81μ showed the absence of free carbonyl groups, i.e. all the extra aldehyde molecules had condensed.

The absorbtion at 2.93μ and 7.72μ might indicate the presence of an alcohol, but this is doubtful as there was nc characteristic absorbtion in the 9.0 - 9.5μ range. The other possibility is that a cyclic ether of sorts had been formed.

An infra red analysis on the acetaldazine compound prepared by Sohn showed a number of similarities, absorbtion occurring at 2.93, 3.75, 6.90, 7.05, 7.21 and 7.72μ.

A further attempt to show that the acetaldazine compounds were similar was made by taking X-ray powder photographs. No characteristic patterns could be obtained however, due to the microcrystalline powder giving very diffuse bands.

While acetophenone gave salts the substituted acetophenones did not. It has been shown[45,46,47] that meta and para substitution in an aromatic nucleus has little effect upon the rate of formation of condensation products, whereas the presence of groups in the ortho positions retards the reaction seriously, regardless of the nature of the substituent -the "ortho or proximity effect".

In the reactions discussed above, however, the azines had been prepared successfully and failure to obtain salts might have been due to hydrogen bond formation (in the case of the ortho-hydroxy compound) or to steric considerations.

Finally, even though simple salts were not obtained from aliphatic ketones, their existence in solution seems probable. Polymerised products were obtained in some cases. In others, impure products were obtained at low temperatures, these decomposed rapidly at room temperature. More recent work done in this department[36] seems to indicate that the acetone ketazinium ion does exist in solution.

CHAPTER III.

FLUOROGALLATES AND FLUOROINDATES OF HYDRAZINE.

(1) The preparation of the halegenogallates and indates.

(i) Hydrazinium chlorides, bromides and iodides of gallium and indium.

The previous salts reported had been made by bringing the components together in dilute acid solution. The complex chlorogallates, chloroindates, bromogallates, bromoindates, iodogallates and iodoindates of hydrazine could not be prepared; in all the preparations attempted the relatively less soluble hydrazinium halides precipitated from solution.

The hydrazinium hexa-chloro-aluminate prepared by Hotz and Pugh[17] has since been examined by means of X-Ray crystallography[69] and it has been shown that the compound is not the complex described; the chlorine atoms not being co-ordinated around the central aluminium ion. The hexa-halides therefore do not appear to exist; the compounds obtained being mixed, hydrated, salts which have co-precipitated from solution.

(ii) Hydrazinium fluorogallates.

The hydrazinium fluorogallates were prepared by a number of different methods viz:

(a) Gallium hydroxide was dissolved in 10% hydrofluoric acid solution, and was then treated with the calculated amount of 10% hydrazine hydrate.

(b) Gallium trifluoride, trihydrate was dissolved in 50% hydrofluoric acid and was then treated with 10% hydrazine hydrate.

(c) Gallium trifluoride, trihydrate was dissolved in 50% hydrofluoric acid and the resulting solution was treated with the stoichiometric amount of hydrazine dihydrofluoride dissolved in water.

(d) Gallium trifluoride, trihydrate was dissolved in 20% hydrofluoric acid and the resulting solution was treated with the stoichiometric amount of hydrazine dihydrofluoride dissolved in water.

(e) Gallium trifluoride, trihydrate was dissolved in 10% hydrofluoric acid and the resulting solution was treated with the stoichiometric amount of hydrazine dihydrofluoride dissolved in water.

(f) Gallium trifluodie, trihydrate was dissolved in water and was then treated with the stoichiometric amount of hydrazine dihydrofluoride.

(g) Gallium hydroxide was dissolved in water and the solution treated with hydrazine dihydrofluoride.

(h) Gallium sesquioxide was dissolved in 50% hydrofluoric acid and was then treated with 95% hydrazine solution.

The majority of the preparations gave compounds of the type sought and their composition is discussed in Section 3 (p. 21).

(iii) Hydrazinium fluorindates.

Generally the fluoroindates were prepared by analagous methods, viz:

(a) Indium trifluoride, trihydrate was dissolved in 10% hydrofluoric acid and the solution was treated with the calculated amount of 50% hydrazine hydrate.

(b) Indium trifluoride, trihydrate was dissolved in 50% hydrofluoric acid and treated with the calculated amount of hydrazine dihyro-fluoride.

(c) Indium trifluoride, trihydrate was dissolved in 10% hydrofluoric acid and treated with the calculated amount of hydrazine dihydrofluoride.

(d) Indium trifluoride, trihydrate was dissolved in water and was treated with the calculated amount of hydrazine dihydrofluoride.

(e) Indium chloride was dissolved in 10% hydrazine hydrate solution and the resulting solution was treated with 50% hydrofluoric acid.

The compounds obtained were very similar to those obtained from gallium and are discussed in section 3 (p. 21).

(2) The determination of fluoride in fluorogallate and fluoroindate.

It was obvious that the estimation of fluoride was of paramount importance in determining the empirical formula of these compounds, and for this reason considerable care was given to the choice of the analytical method finally used (see analytical methods, p. 41).

Five methods were considered:

(i) Precipitation as lead chloro-fluoride
(ii) Precipitation as calcium fluoride
(iii) Precipitation as lanthanum fluoride
(iv) Titration with thorium nitrate
(v) High frequency titration using lanthanum acetate.

Method (ii) was rejected as the precipitate obtained is very difficult to handle. The other methods were all tested, using pure gallium trifluoride, trihydrate. [The lead chloro-fluoride method was found to be the most suitable even though the precipitate is relatively soluble (370 mg/litre) and the method is known to be subject to errors of as much as 3%].

(3) Composition of the Fluorogallates and fluoroindates of hydrazine.

In all but a few cases, where for some inexplicable reason the hydrazine content was very low, compounds of the type sought were found. Only once was crystalline product obtained, the other preparations yielding, generally, amorphous powders and in a few instances vitreous glass-like product.

The crystalline product was the hydrated penta-fluorogallate sought. The crystals were far too small for X-Ray analysis but could be examined under the polarising microscope where they showed straight extinction. A large number of fan-like multiple crystals were present in the crop. These two properties show that definite symetry exists in the crystal structure.

Also prepared were the anhydrous dihydrazinium hexafluorogallates and indates and a number of hexa-fluorogallates and -indates with extra HF present. The compounds with the extra HF could be grouped into three categories, those with 2-3; 9-11; and 14 molecules of HF extra. If stored under vacuum for some time the compound with 14 molecules of HF extra lost three molecules, the desiccator becoming very severely etched in the process.

To see whether the ability to hold extra HF was a property of the complex only, attempts were made to prepare hydrazine dihydrofluoride and gallium trifluoride with extra HF present. Hydrazine is known to form a mono and a difluoride. A large number of preparations were undertaken and in no case was a hydrazinium compound found with more than two fluorine atoms. Gallium trifluoride was prepared from gallium metal, from gallium hydroxide, from gallium nitrate and from gallium sesquioxide (a number of times from each starting material) and in only one case was a gallium compound with more than three fluorine atoms isolated. This compound was $GaF_3.3H_2O.HF$; the extra molecule of HF being lost very easily on storing the compound under vacuum.

(4) Investigation of the complex salts by physical methods.

The problem of the extra molecules of hydrogen fluoride required consideration. The extra molecules might have been adsorbed on the surface, hydrogen fluoride being known to form chains up to about $(HF)_6$ with bond angle 140°[58]. On the other hand metal fluorides are often solvated by hydrogen fluoride, and the extra molecules might have been held in this manner. A number of series of such solvated compounds are known, potassium forming the series KF, KF.HF, KF.2HF, KF.3HF, KF.4HF and 2KF.5HF[59]; rubidium forming the series RbF. 2HF. RbF. 3HF. and RbF. 3.5HF; and caesium forming the series CsF. HF, CsF.2HF, CsF.3HF, and CsF. 6HF.

(i) Spectroscopic methods.

Compounds with one or two molecules of hydrazine had been prepared. Two alternative formulations therefore offered themselves. Either the "complex" anion was GaF_6^{2-} with either one $N_2H_6^{2+}$ or two $N_2H_5^{+}$ ions present, or it was GaF_4^{1} in some cases and GaF_5^{2-} in others with hydrazine always present as the $N_2H_5^{+}$ ion.

The Raman spectrum of hydrazine dihydrochloride[62] reveals a very sharp and intense line at 1036 cm^{-1} assigned to the $N_2H_6^{2+}$ ion, flanked by two weaker and broader lines at 968 cm^{-1} and 1110 cm^{-1} arising from dissociation of the $N_2H_6^{2+}$ ion to the $N_2H_5^{+}$ ion. The spectrum of hydrazine mono-hydrochloride reveals only the latter lines with no trace of the line at 1036 cm^{-1}. A study of the Raman spectra of the compounds under investigation, it was thought, would show which species was present.

Facilities for Raman spectrum investigation were not available. A Hilger D77 constant deviation spectroscope with reasonable dispersion in the range required was available, however, and attempts were made to adopt this instrument for Raman analyses. A special camera, suitable for Raman work, to fit the spectroscope was obtained from Hilger and Watts Ltd., and it was felt that this with Kodak Type Oa-O plates (maximum sensitivity in the spectrum range under investigation, and with best light gathering capabilities for exposures of one minute or longer) might prove adequate. A high intensity mercury lamp with its controls was built in the laboratory and used as a light source[72]. (See Fig. 2, p. 101).

No successful exposures were made however, and no information could be obtained. Facilities for Raman investigation subsequently became available at the National Physical Laboratories, Pretoria, and a sample of the crystalline hydrazinium pentafluorogallate was sent to them for examination. They were unable to obtain a sufficiently concentrated solution to enable the spectra to be taken.

(ii) Conductimetric titrations and molar conductances.

(a) Attempted determination of free HF.

Webb and Prideaux[60] while investigating the acid fluorides of Rubidium had determined free HF using ammonium hydroxide in carbon dioxide-free water with bromo-thymol-blue as indicator.

An approximately $^{N}/_{50}$ solution of ammonium hydroxide was made by passing pure ammonia gas through carbon dioxide-free distilled water.

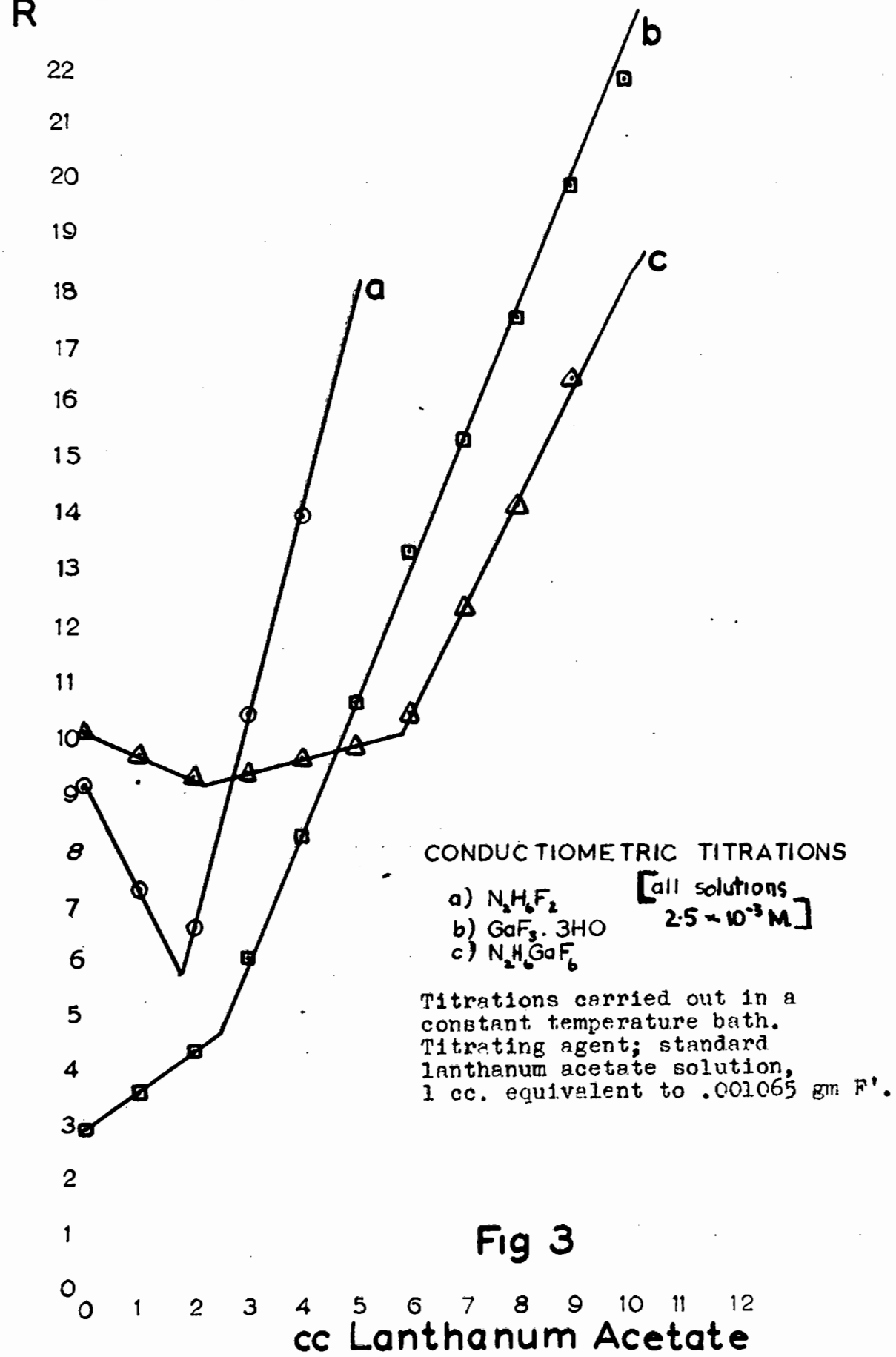

1/R x 10⁴ mhos
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0 1 2 3 4 5 6 7 8 9 10 11 12
cc Lanthanum Acetate
a
b
c
CONDUCTIOMETRIC TITRATIONS
a) N₂H₆F₂
b) GaF₃. 3HO
c) N₂H₆GaF₆
[all solutions 2·5 × 10⁻³ M.]
Titrations carried out in a constant temperature bath. Titrating agent; standard lanthanum acetate solution, 1 cc. equivalent to .001065 gm F'.

Fig 3

a combination of the previous two, the conductance dropping initially, then rising and finally increasing at a greater rate.

The break in the hydrazine dihydrofluoride curve occurs at the theoretically expected value. The break in the gallium trifluoride trihydrate curve occurs at 2/3 of the theoretical expected value indicating that two of the fluorides are behaving differently from the third, i.e. an ionic species GaF^{2+} appears to remain. With the complex hexa-fluorogallate the first break corresponds to two fluoride ions, i.e. to the hydrazine dihydrofluoride while the second is equivalent to a further three fluoride ions also indicating that one atom remains associated with the gallium atom, i.e. GaF^{2+}.

This agrees with previous work[64] gallium being known to form complex ions in solution in the presence of fluoride, the majority of the metal being present as GaF^{2+} according to the following relationship:-

$$\frac{[GaF^{2+}]\ [H^+]}{[Ga^{3+}][HF]} = 1.2 \times 10^2$$

A very small percentage of the gallium will be present as the hydrated ion according to the relationship

$$\frac{[Ga(OH)^{2+}]\ [H^+]}{[Ga^{3+}]} = 1.2 \times 10^{-4}$$

and some of the fluoride will be associated to HF, HF_2^- and $H_2F_3^{2-}$. The presence of all these species naturally affects the precise values obtained in the titrations.

(c) Molar conductances.

The molar conductance at infinite dilution of gallium trifluoride and of the hexa-fluorogallate were determined at 25°C.

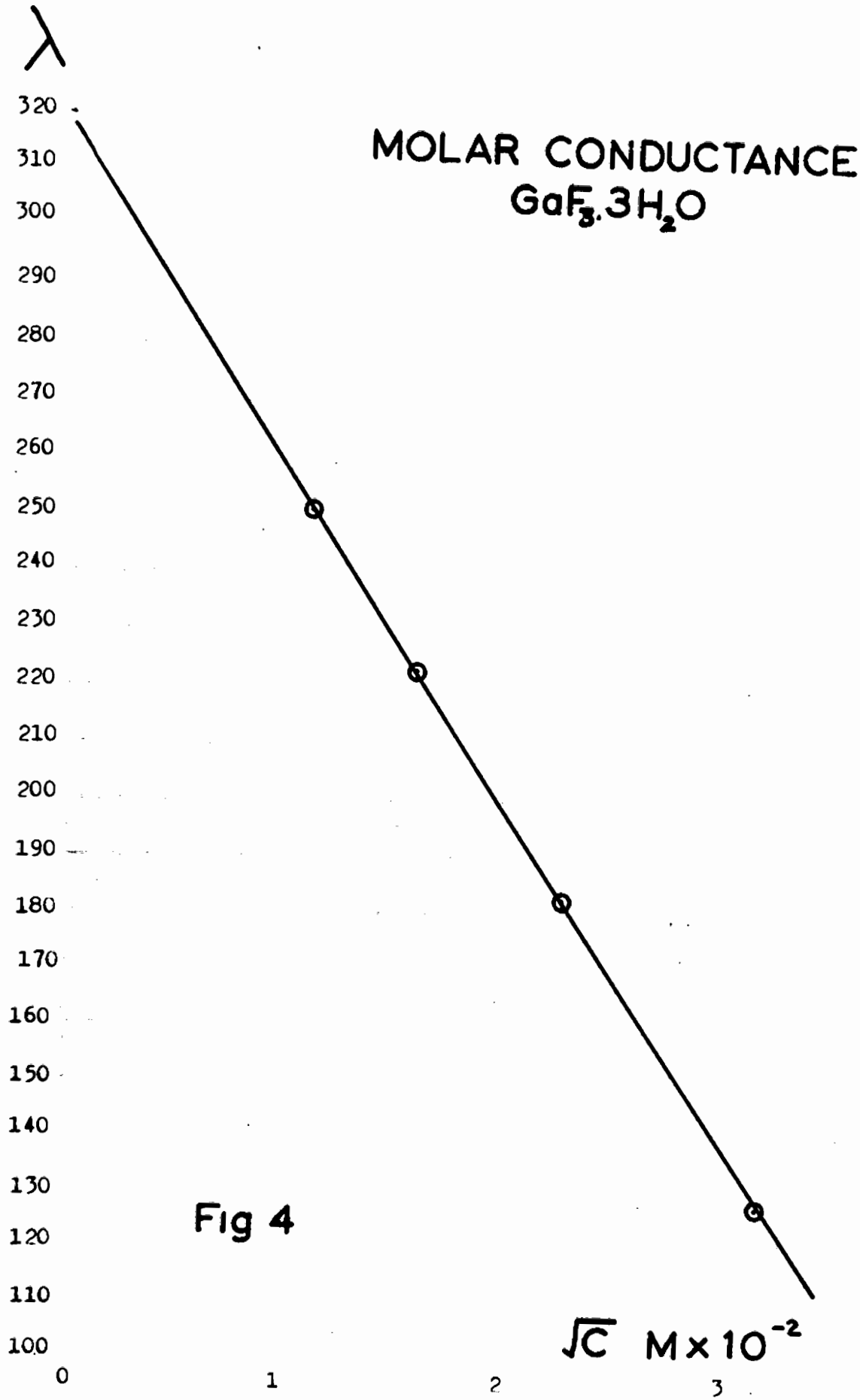

λ
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
0
1
2
3
√C M×10⁻²
MOLAR CONDUCTANCE
GaF3.3H2O

Fig 4

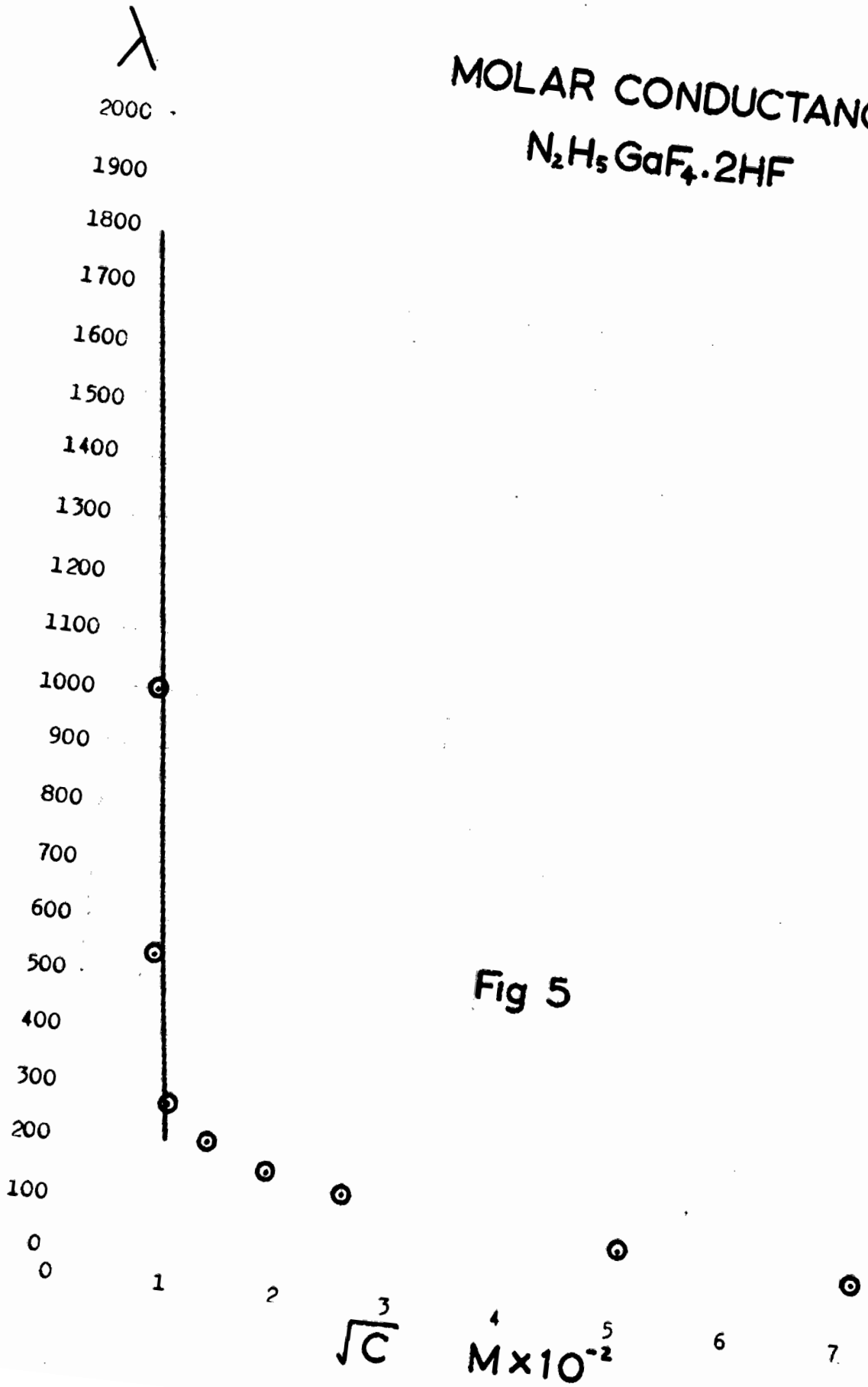

λ
MOLAR CONDUCTANCE
$N_2H_5GaF_4.2HF$
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7
$\sqrt{C}$
$M \times 10^{-2}$

Fig 5

(See Figs. 4 and 5).

The value obtained from the trifluoride could not be checked against that required theoretically as no data could be found with respect to the conductivity of the gallium ion. It could be assumed, however, that the conductivity of GaF^{2+} must be less than the conductivity of Al^{3+}, i.e. is of the order of 50 $ohm^{-1} cm^2$. Davies[74] gives a value for the fluoride ion of the order of 150 $ohm^{-1} cm^2$.

Assuming that in solution we get $GaF_3.3H_2O \rightleftharpoons GaF^{2+} + 2F^- + 3H_2O$ we would expect a value of the order of 350 $ohm^{-1} cm.^2$. The observed value 320 $ohm^{-1} cm^2$ is in reasonable agreement, bearing in mind the other species which might be present (see (b) above).

Irrespective of the actual value, however, we can assume that in determining the molar conductance of the hexa-fluorogallate, the gallium will behave in the same way.

The curve for the complex followed the pattern normally shown by hydrazine complexes, i.e. a gradual increase in λ with a sudden increase at very low concentrations[36] giving the molar conductance at infinite dilution approximately 1800 $ohm^{-1} cm^2$.

Taking a value of 320 $ohm^{-1} cm^2$ for the gallium and three fluorides, 150 $ohm^{-1} cm^2$ for fluoride, 350 $ohm^{-1} cm^2$ for the hydrogen ion and 70 $ohm^{-1} cm^2$ for the $N_2H_5^+$ ion[36] we obtain a value of 1900 $ohm^{-1} cm^2$ if we assume the presence in solution of three hydrogen fluoride molecules. This indicates that the complex is more likely to be $N_2H_5GaF_4 . 2HF$ than $N_2H_6 GaF_5 HF$, the following reactions occurring on solution.

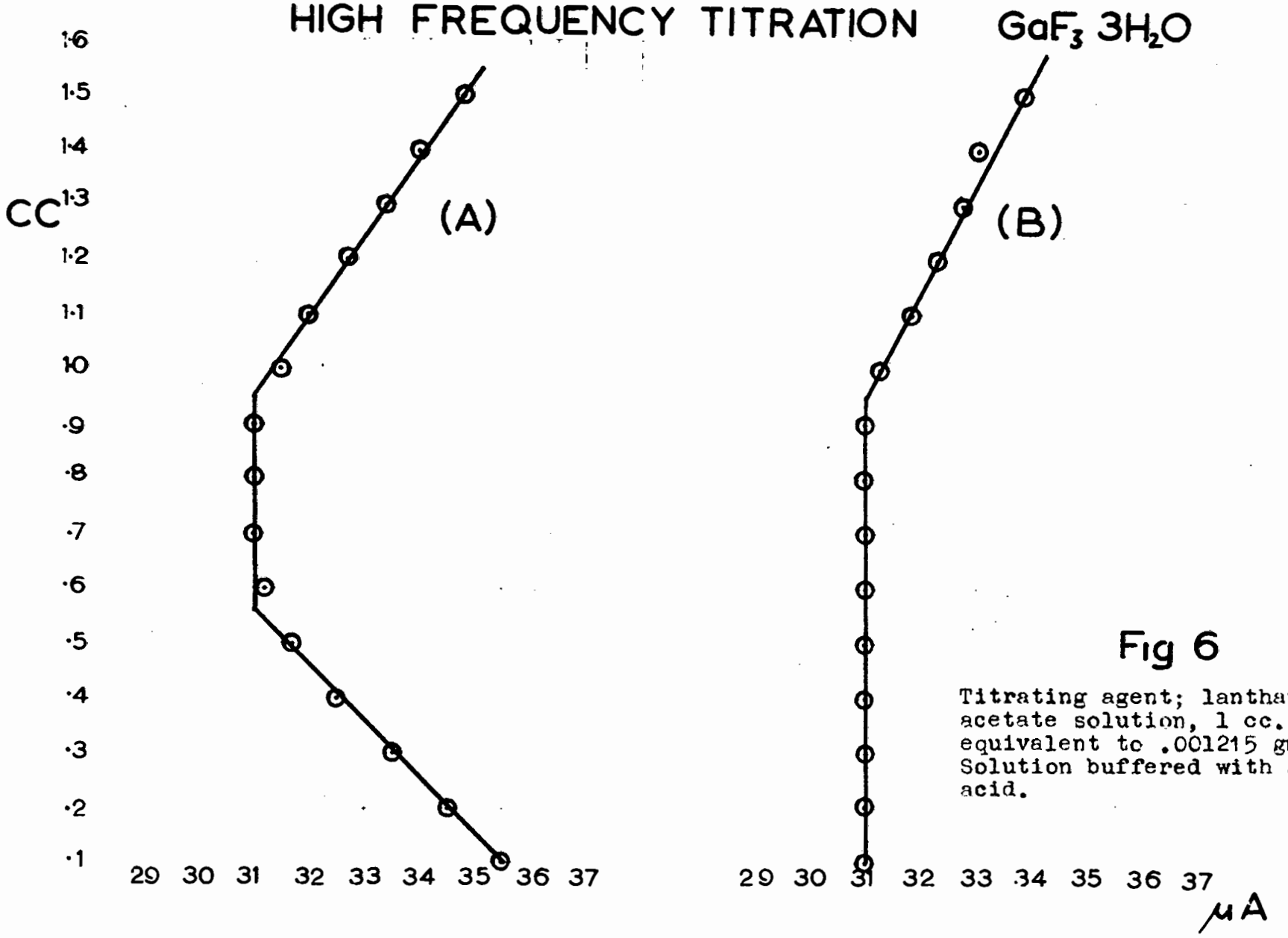


Fig 6

Titrating agent; lanthanum acetate solution, 1 cc. equivalent to .001215 gm. F'. Solution buffered with acetic acid.

$$N_2H_5\ GaF_4\ 2HF \rightleftharpoons N_2H_5^+ + GaF_4^- + 2HF$$

$$GaF_4^- \rightleftharpoons GaF_3 + HF$$

$$GaF_3 \rightleftharpoons GaF^{2+} + 2F^-$$

(iii) High frequency titrations.

A High Frequency Titrimeter as described by Dowdall, Sinkinson and Stretch[65] was constructed, and the titrations were carried out as described by them, viz: using lanthanum acetate as titrating agent, the solution being buffered with acetic acid. The lanthanum acetate was standardised against sodium fluoride. A series of titrations were carried out on hydrazine dihydrofluoride solutions. The curves obtained were similar to those obtained with sodium fluoride (current decreased until equivalence point was reached and then increased) and the break corresponded to the total fluoride present.

The curves obtained with $GaF_3 . 3H_2O$ are shown on Fig. 6.(A) was a 2.2×10^{-3} M solution (required 3 c.c. of reagent). Two breaks occurred having the ratio 2:1, the final break occurred at 1/3rd the value expected, indicating the formation of a complex ion according to the relationship

$$GaF_3 \rightleftharpoons CaF_2^+ + F^-$$

Of interest is the vertical portion of the curve. The basis of these titrations is very complex and is by no means understood, consequently no explanation can be offered for this vertical portion of the curve. A possibility exists that in this range the gallium complex and the lanthanum fluoride behave in the same manner under the conditions of the titration.

HIGH FREQUENCY TITRATION $N_2H_5GaF_4.2HF$

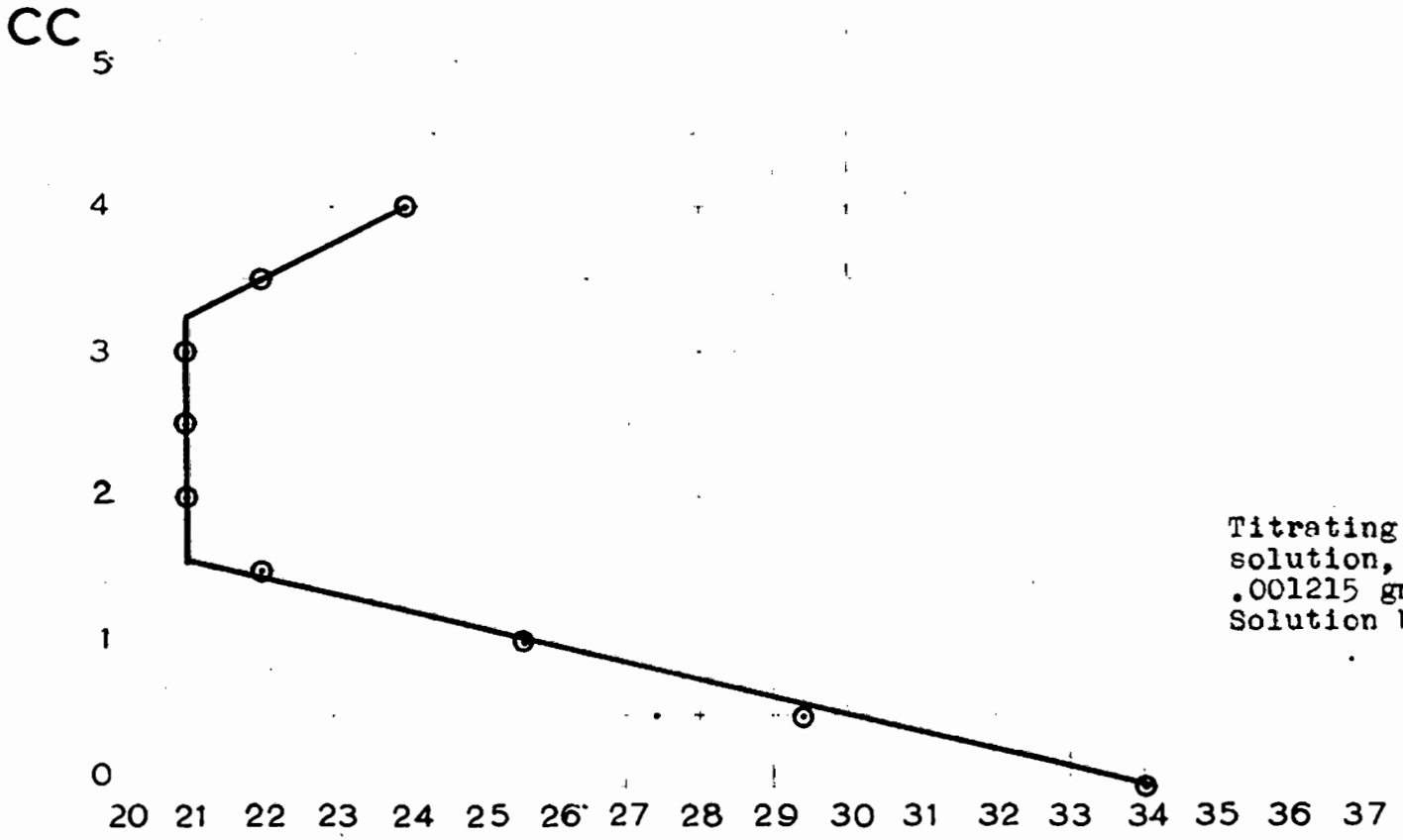


Fig 7

Titrating agent, lanthanum acetate solution, 1 cc. equivalent to .001215 gm. F'.
Solution buffered with acetic acid.

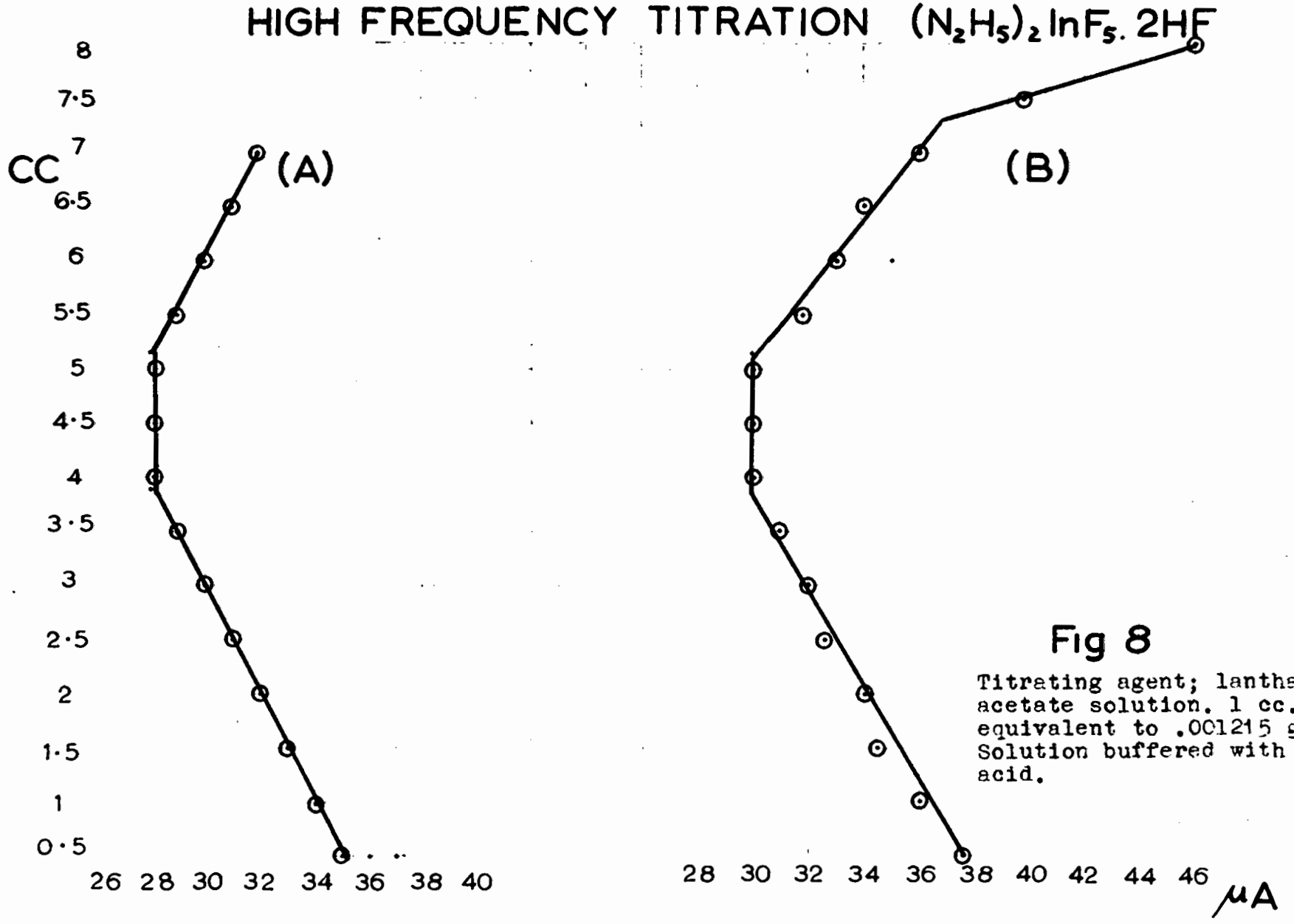


Fig 8

Titrating agent; lanthanum acetate solution. 1 cc. equivalent to .001215 gm. F'. Solution buffered with acetic acid.

Curve (B) is for a solution of twice the previous concentration i.e. 4.4×10^{-3} M. The first break disappeared and there was no change in the final titration figure. This indicated that only half a molecule of fluoride had reacted. Possibly in this concentration the gallium trifluoride is more stable than lanthanum fluoride.

Titrating the complex $N_2H_5\ CaF_4\ 2HF$ gave the curve shown on Fig. 7. Here the curve initially followed the expected course, then rose vertically as with the gallium trifluoride, trihydrate and finally the current increased steadily with addition of the lanthanum reagent. The two breaks again were in the ratio 1:2 and the end point was 2/3 of that theoretically required, indicating that only four fluorides had reacted in two stages, i.e.

$$N_2H_5\ GaF_4\ 2HF \rightarrow N_2H_5^+ + GaF_4^- + 2HF$$

$$GaF_4^- \rightarrow GaF_2^+ + 2F^-$$

Fig. 8. Shows the titration curves for the complex $(N_2H_5)_2$. $In\ F_5 . 2HF$ Curve (A) was determined on solution. Two breaks were again recorded, the final value being 5/7th of that expected, indicating once more a two stage breakdown leaving a complex $In\ F_2^+$.

$$(N_2H_5)_2\ In\ F_5 . 2HF \rightarrow 2\ N_2H_5^+ + 2HF + 2F^- + In\ F_3$$

$$In\ F_3 \rightarrow In\ F_2^+ + F^-$$

Curve (B) was recorded after the solutions had stood for three weeks. Here a third inflection was obtained at the expected value. It seemed that on standing the complex had dissociated

$$InF_2^+ \rightarrow In^{3+} + F^-$$

The final titrations were done on a solution 2.5×10^{-3} M of the

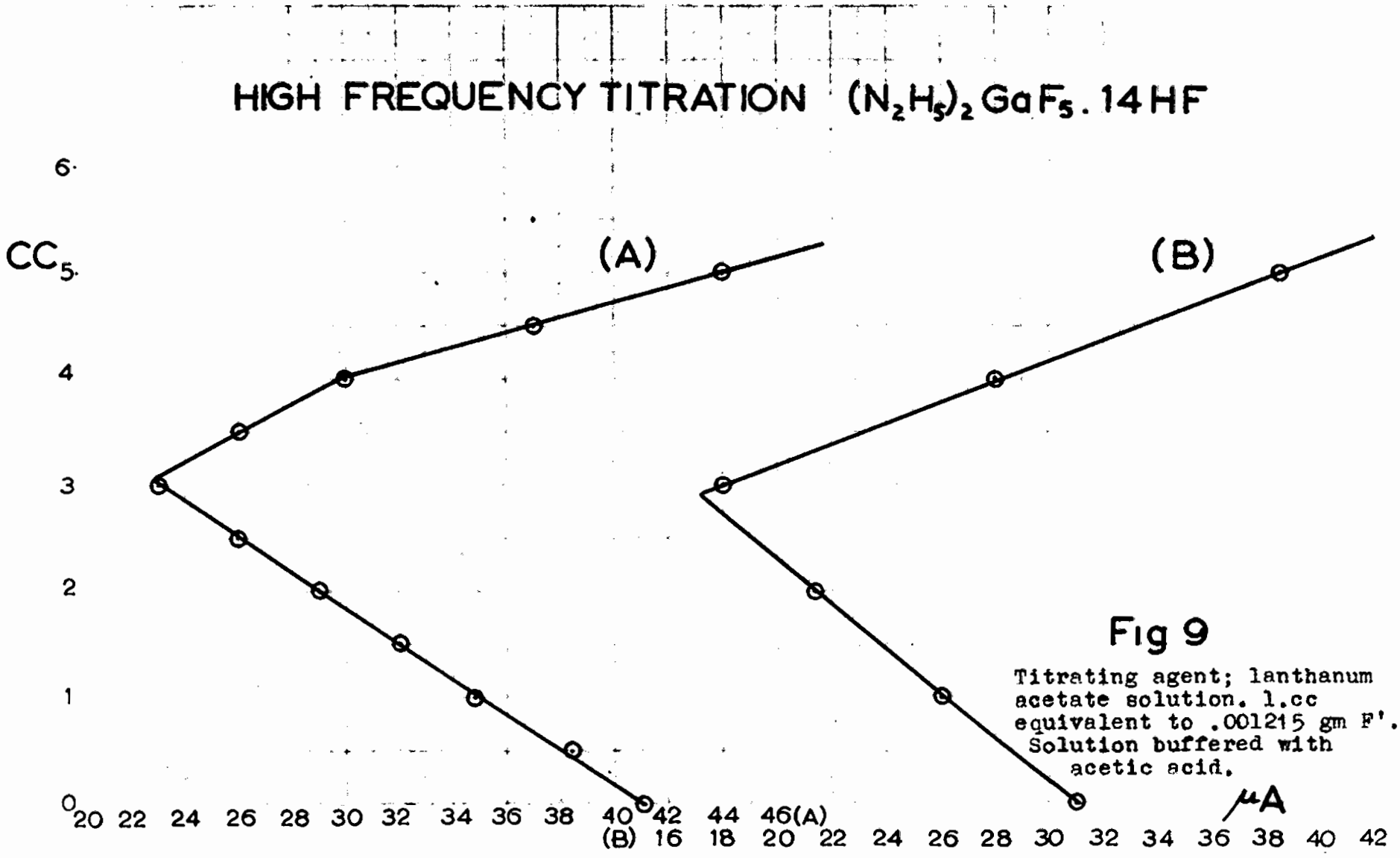


Fig 9

Titrating agent; lanthanum acetate solution. 1.cc equivalent to .001215 gm F'. Solution buffered with acetic acid.

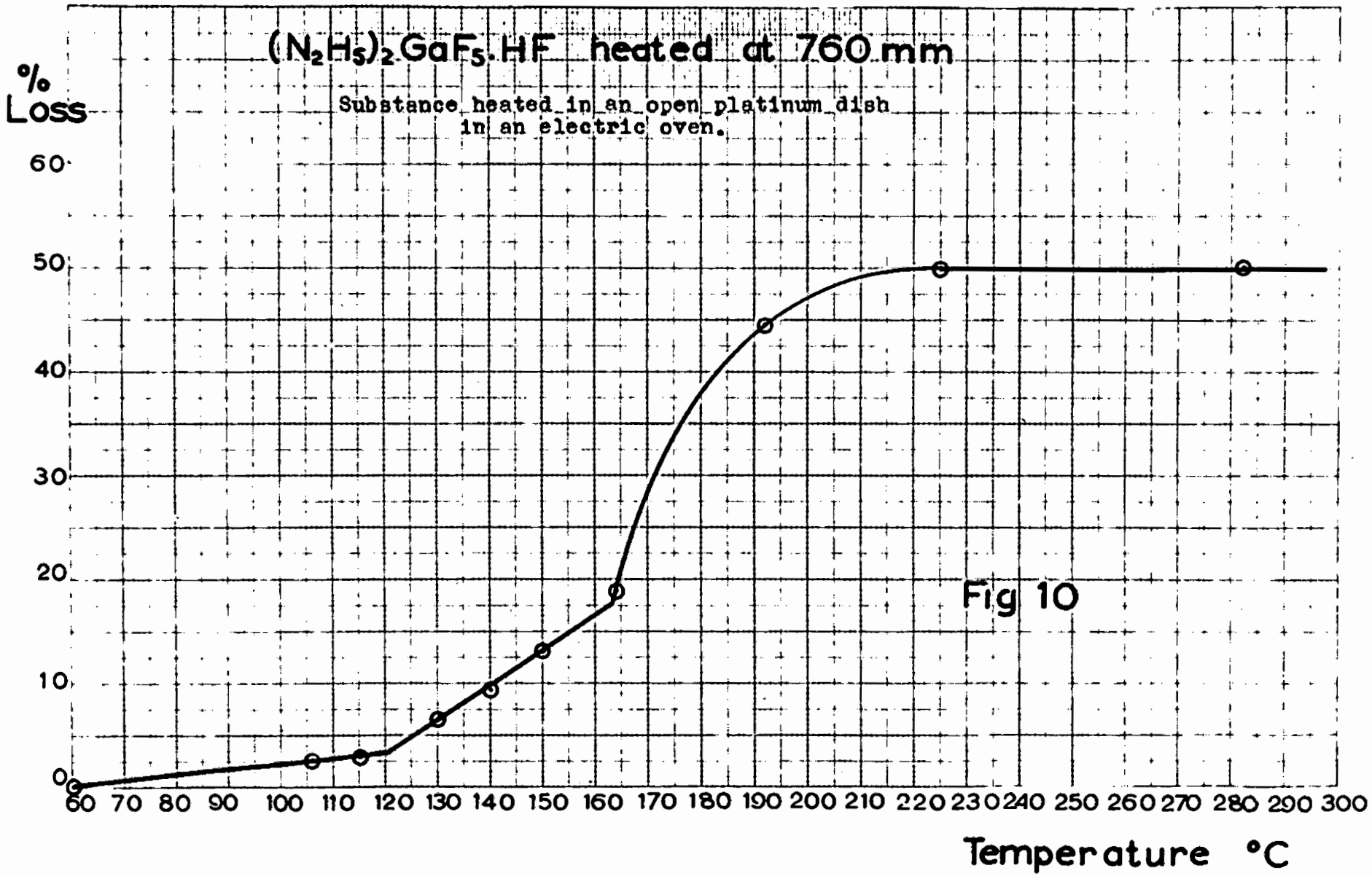

$(N_2H_5)_2GaF_5.HF$ heated at 760 mm
Substance heated in an open platinum dish in an electric oven.
% Loss
60
50
40
30
20
10
0
60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300
Temperature °C

Fig 10

complex with 14 extra molecules of hydrogen fluoride. $(N_2H_5)_2$ GaF_5 14HF. (Fig 9)

Here Curve (A) was determined on solution and had two breaks with no vertical portion. The breaks were in the ratio 3:4 but the final figure only corresponded to 11 fluorides. No explanation could be found for this. Curve (B) was determined after the solution had been allowed to stand for three weeks. Here instead of getting a higher titration figure, the second break in the curve disappeared altogether. It is possible that the relatively higher concentration of fluoride (with some chance of HF complexing) had something to do with these results.

(iv) Thermal decomposition.

The potassium acid fluorides were investigated by Cady[66], who treated them, in a closed copper container, with anhydrous hydrogen fluoride. The compounds formed were not separated or examined but their existence was confirmed from the nature of the curve of initial freezing points and the calculated compositions of the mixtures.

Ruff and Staub[75] investigated the ammonium acid fluorides. They used an open system adding various quantities of hydrogen fluoride to ammonium bifluoride, and obtained evidence of the existence of the complexes by means of an approximate thermal diagram.

The acid fluorides of rubidium were very extensively investigated by Webb and Prideaux[60]. Initially they added HF to the system being investigated and plotted the cooling curves. They also expelled HF by

heating the mixture at the appropriate temperature. The rate of loss of weight gave just as satisfactory information as the previous method; changes in direction of the curve giving results which agreed with those found from the cooling curves.

The caesium fluoride-hydrogen fluoride system was investigated by Windsor and Cady[61] who also determined cooling curves.

Einecke[68] had reported that the compound $(NH_4)_2\ GaF_5$ could be converted to $NH_4\ GaF_4$ by heating; it seemed likely, therefore, that some information about the fluorogallates could be obtained by investigating their thermal decomposition.

The first compound to be heated was the complex $(N_2H_5)_2\ GaF_5.HF$. This was heated in an open platinum dish in an oven, the dish and contents being weighed hourly. No change in weight for five successive weighings was considered sufficient to assume constant weight. The curve "Loss of weight against temperature" is shown on Fig. 10. There are two straight line portions indicating loss first of HF and then of hydrazine and HF to give the $N_2H_5\ GaF_4$ x HF compound. Finally there is a continuous curve as the complex breaks down to form GaF_3.

Similarly, heating the compound with 14 extra HF molecules, gave the curve shown on Fig. 11. There are two distinct breaks one at 12% loss and the second at 34%. If all the loss is due to HF the first break corresponds to the loss of 3HF and the second to 8.5 HF. The first result agrees with earlier results (14 HF → 11 HF on being stored under vacuum), the second break indicates a compound with

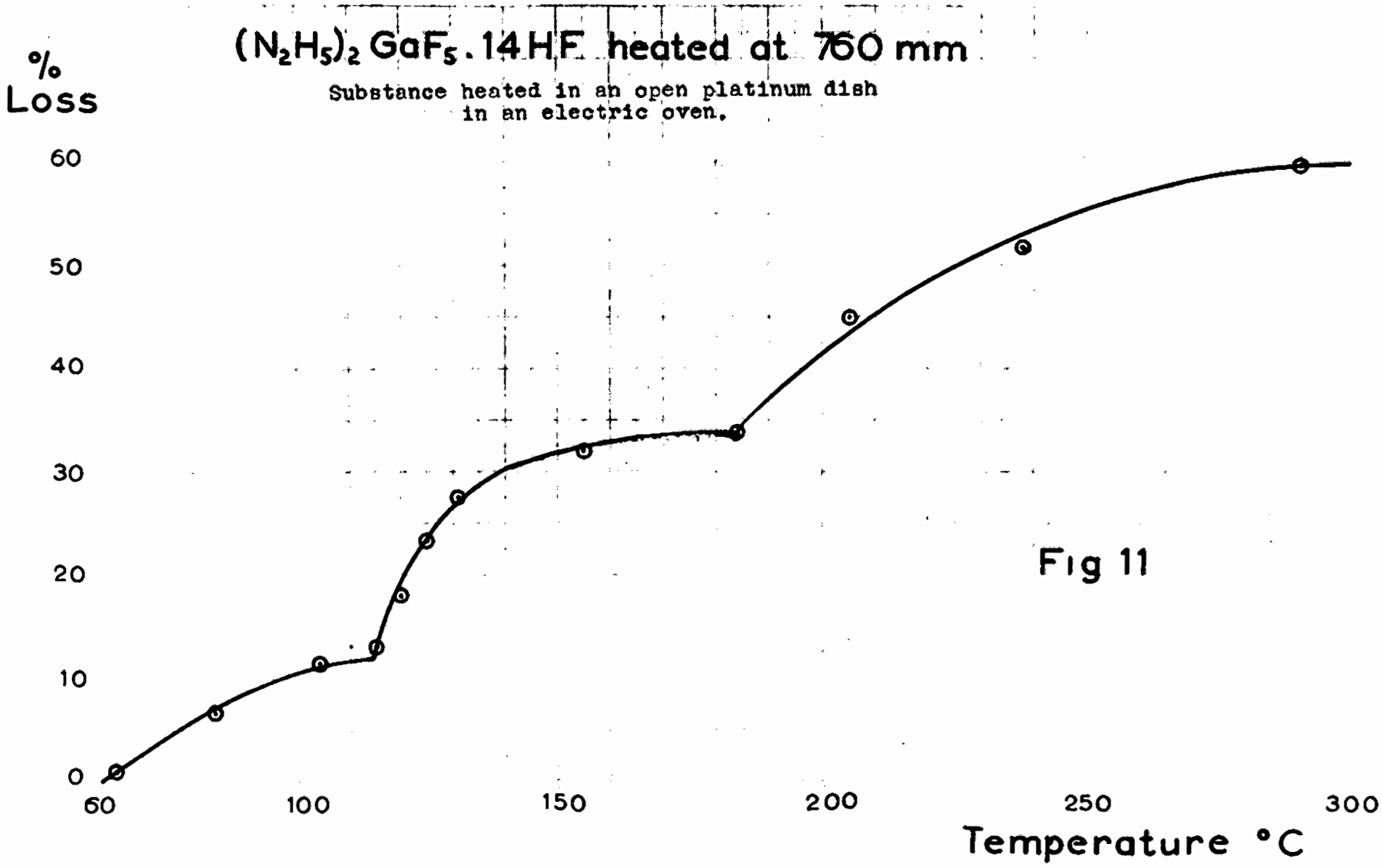

$(N_2H_5)_2 GaF_5 . 14HF$ heated at 760 mm
Substance heated in an open platinum dish in an electric oven.
% Loss
60
50
40
30
20
10
0
60
100
150
200
250
300
Temperature °C

Fig 11

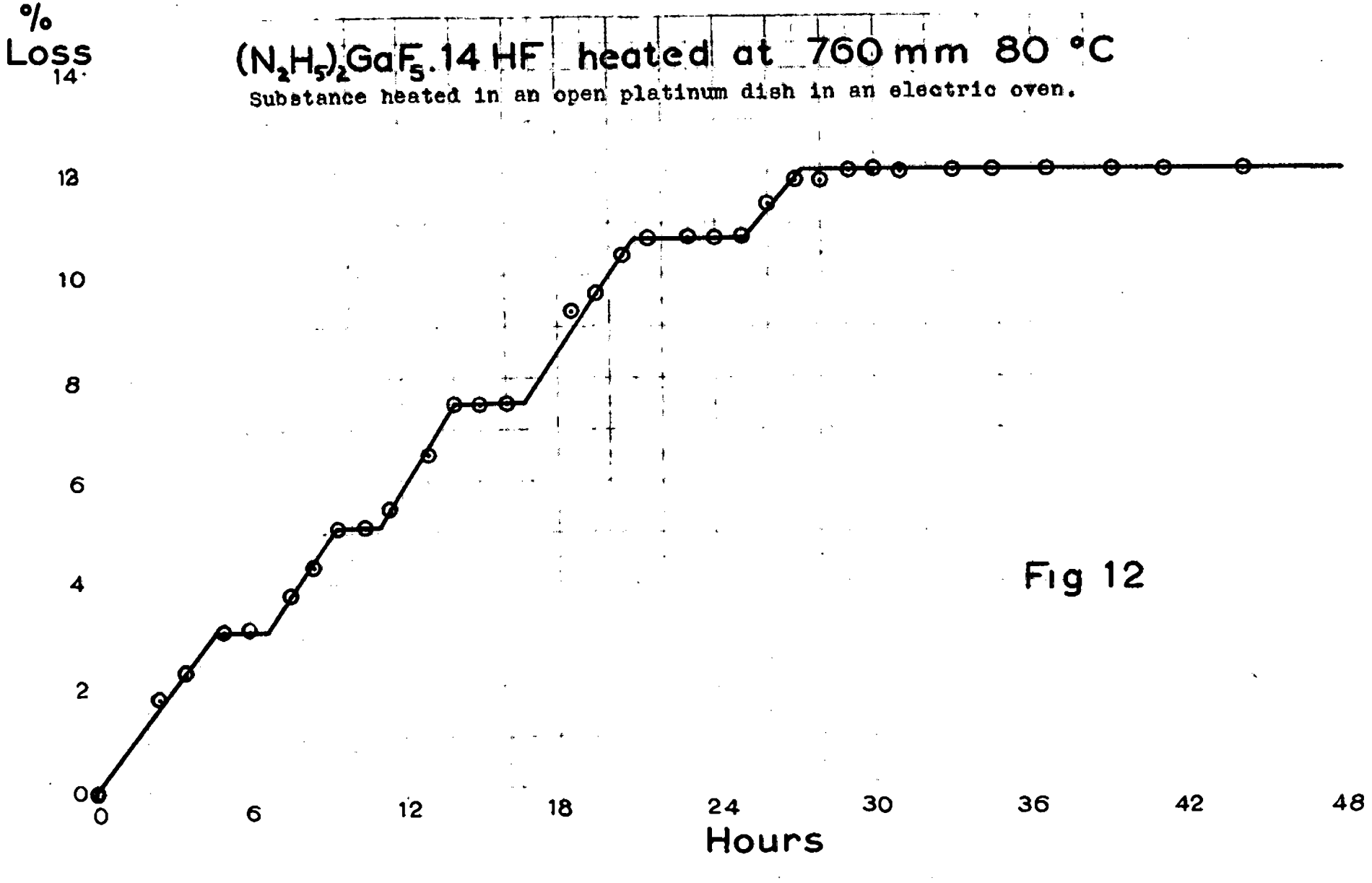
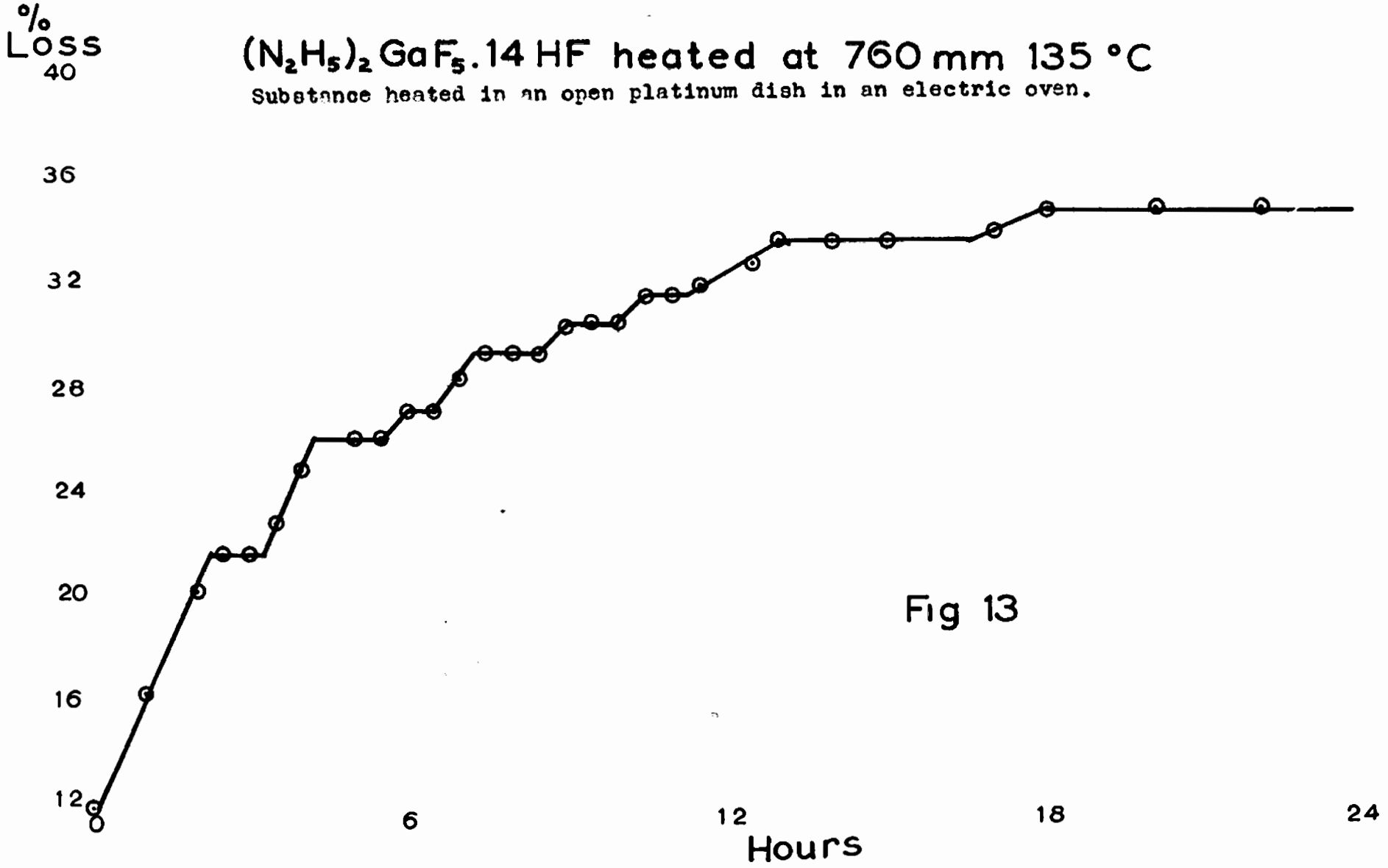

% Loss
$(N_2H_5)_2GaF_5.14\,HF$ heated at 760 mm 80 °C
Substance heated in an open platinum dish in an electric oven.
14
12
10
8
6
4
2
0
0
6
12
18
24
30
36
42
48
Hours

Fig 12



$(N_2H_5)_2GaF_5.14\,HF$ heated at 760 mm 135 °C

Substance heated in an open platinum dish in an electric oven.

Fig 13

6 extra HF molecules present. Such a compound was not found. However this portion of the curve flattens out in the region of 150°C and it is possible that hydrazine is coming off as well.

Fresh samples of the compound were heated, this time at constant temperature and the rate of loss of weight was plotted.

The results of these experiments are shown on Figures 12, 13 and 14. Fig. 12 shows the result of heating at 80°C at atmospheric pressure. Regular steps were observed at what appeared to be multiples of 5%; 4% being approximately one molecule of HF. At 12% loss in weight the loss of HF ceased and the compound attained constant weight. This is equivalent to 3 molecules of HF and agrees with the results found by analysis and with the first break in the curve on Fig. 11. The temperature was increased at 135°C and the curve shown on Fig. 13 was obtained. Here there are also stepwise breaks, at irregular values, however. The curve becomes horizontal at approximately 34% loss in weight. This agrees with the second break in the curve shown on Fig. 11. The temperature was again increased (to 238°C) and the curve given on Fig. 14 was obtained. Here there was only one arrest, otherwise there was a regular loss in weight. These curves were redetermined under reduced pressure (40 mm., 80°C); initially the loss was more rapid than under atmospheric pressure, as was to be expected, and a number of arrests in the curve were not obtained. No arrest point was found in the region of 12% but the curve flattened out in the neighbourhood of 28 - 32%. (See Fig. 15)

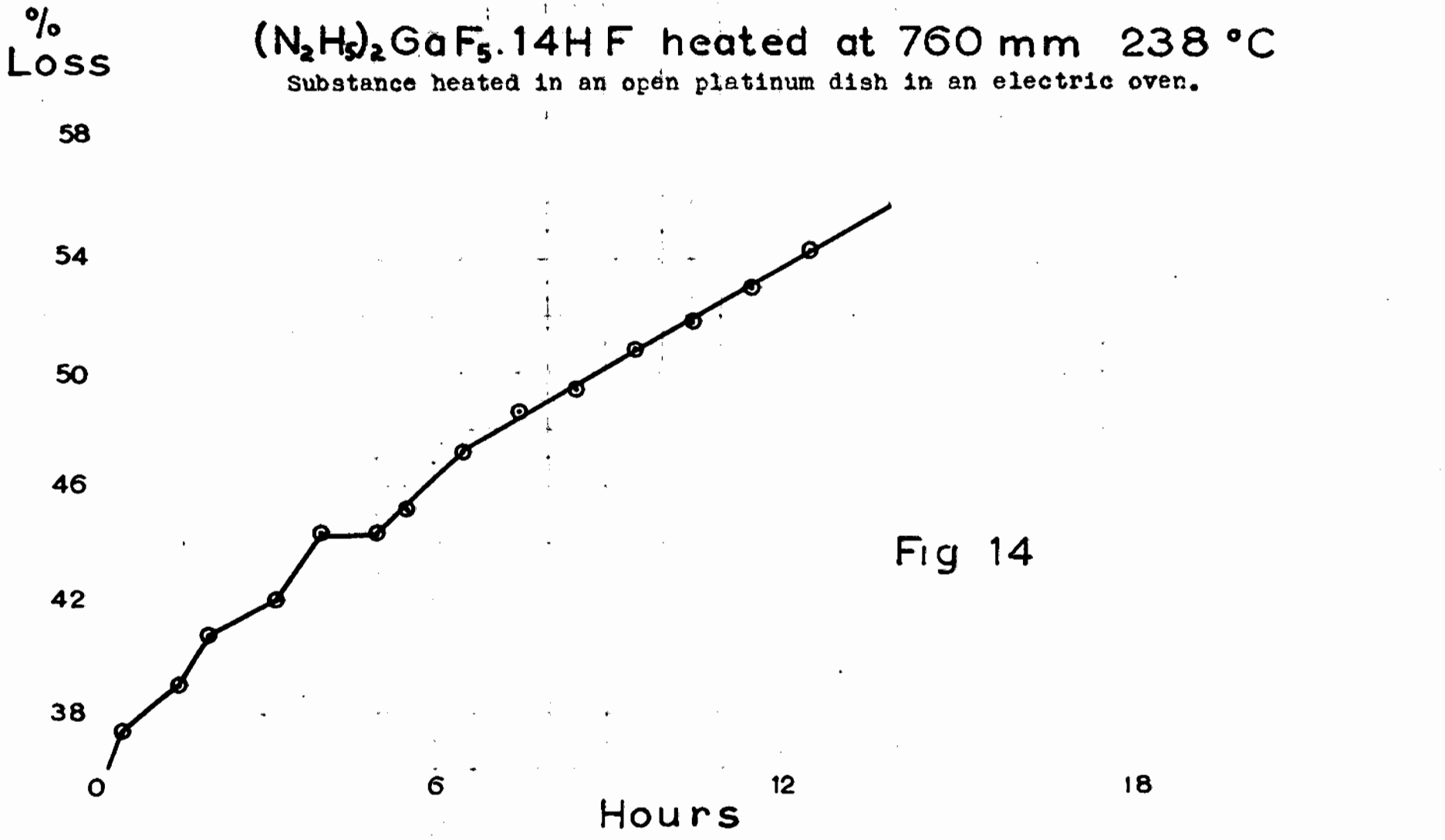

% Loss
$(N_2H_5)_2GaF_5.14HF$ heated at 760 mm 238 °C
Substance heated in an open platinum dish in an electric oven.
58
54
50
46
42
38
0
6
12
18
Hours

Fig 14

This last curve was determined with the sample in a boat made from polythene tubing. During the heating this boat became coloured due to depolymerisation. The effect of heating this tubing was investigated, no significant change in weight was noted, however.

Samples were taken at different stages and analysed for hydrazine and gallium. Under 12% loss the hydrazine:gallium ratio was 2:1, from this point hydrazine began to be lost as well, giving a 1:1 ratio by the time the 34% point had been reached. Thereafter the second hydrazine began to come off as well. This explains the variation in the size of the steps, and there being no relationship to the number of molecules of HF. These experiments indicate therefore that 3 molecules of HF are relatively lightly held and can be lost easily. The remainder are more strongly bound and the complex itself decomposes before they are lost. It would therefore seem that these compounds with a large excess of fluoride are definite compounds and that the excess is not there as adsorbed HF.

(5) General discussion of the fluorogallates and fluoroindates.

(i) Structure of the complex.

Weinland had reported the existence of amorphous hydrazinium fluoroaluminate[12], whereas Hotz and Pugh[17] obtained it as a crystalline substance. The fluorogallates and fluoroindates reported in this thesis were generally obtained as amorphous substances, although on some occasions vitreous product was obtained. Once a crystalline fluorogallate was prepared.

Wells[76] states that similarity in formula type does not necessarily

mean similarity in structures. Compounds of the type A_mBX_n, assuming that all the atoms of each kind have similar environments in the crystal, may be grouped into a number of classes. There seems little doubt that the fluoroaluminates belong to the class where B and X form finite complexes (BX_n) of one kind only and can be described in terms of AlF_6 octohedra.

Theoretically one would expect the fluorogallate to be similar. Consideration of the maximum co-ordination number with reference to the charge on the central ion, and consideration of the critical ratio of the radii of the Ga^+ and F^- ions indicated that there should be five or six fluorine atoms around the central gallium atom in the fluorogallates. Moeller[77] lists a complex ion $(GaX_6)^{3-}$.

While this finite complex might be present in the crystalline product (the Physics Department of the University of Cape Town were approached with a view to examining the structure of the crystals, which proved too small, however, for X-Ray diffraction studies) it does not seem likely in the amorphous powder.

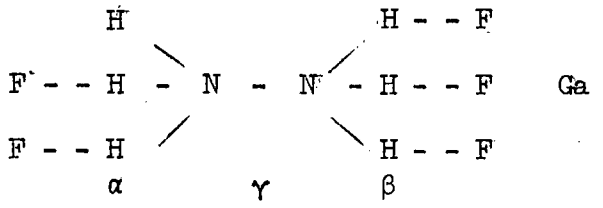
Audrieth[78] has discussed the structure of the hydrazine molecule. It seems probable that the molecule exists in the form shown below, with bond angles 108 $\pm$ 10 degrees.

(a) (b)

Structure of hydrazine molecule.

(a) in perspective (b) with N-N axis perpendicular to the plane of the page.

The gallium trifluoride molecule is planar in shape, and it seems feasible that the hydrazine can be joined to two hydrogen atoms and thence to two fluorine atoms by hydrogen bonding; and that it can simultaneously be attached to the gallium trifluoride molecule by hydrogen bonding. This arrangement is shown schematically below:



There are three types of linkage α, β and γ. α and β could be on either nitrogen but γ is assymetrical. We can therefore get the following configurations:

α - γ - α

α - γ - β

β - γ - α

β - γ - β

The middle two being the same form.

There could be a statistical arrangement of these three forms as with the silicates. This would explain the lack of crystalline product and also the formation of vitreous product on occasion, when the solutions were evporated to dryness. Whether the crystalline or amorphous form precipitates might depend on the relative amounts of gallium, hydrazine and fluorine present, or on the temperature of the solution. There is insufficient information at the moment, however, to hazard a guess.

(ii) Nature of the complex.

The results of the thermal decomposition experiments indicate very strongly that the extra fluorine is interstitially held and not merely adsorbed on the surface of the complex.

The complex anion is most likely GaF_4^- with the hydrazine present as $N_2H_5^+$. This agrees with the Raman work of Woodward and Bill[79] and of Woodward and Nord[80] which shows the existence of the complex ions $InBr_4^-$ and $GaBr_4^-$ in solution. On standing this complex appears to dissociate to give GaF^{2+} and $3F^-$.

In the compounds with more than one hydrazine molecule the basic complex appears to be $(N_2H_5)_2GaF_5$. This agrees with the ammonium fluorogallates reported by Einecke[68] where both NH_4GaF_4 and $(NH_4)_2GaF_5$ were found, the latter decomposing to give the former on being heated.

CHAPTER IV.

EXPERIMENTAL.

(1) Starting materials.

The aldehydes and ketones used were in the majority of cases obtained from reputable manufacturers of chemicals and were used as supplied. Where the source of supply did not give the purity (e.g. the acetone and ethylmethyl ketones were commercial grade) the ketones were redistilled and the correct boiling point fraction utilised.

The azines mentioned in the literature had been made by condensing the amine with the carbonyl compound[18]; by treating the aldehyde or ketone (kept below 10°C) with hydrazine hydrate and then drying the product with potassium carbonate[19] or by adding the ketone (in a suitable solvent) to a warm solution of hydrazine sulphate and sodium carbonate in water[20]. With the availability of concentrated hydrazine solutions it seemed likely that direct condensations would take place. This was found to occur in some cases. Subsequent to the work discussed in the first section of this thesis being completed, a similar technique was reported with regard to the synthesis of some ketazines and thio-semi-carbazones[21]. When solid, the azines were recrystallised; ;iquids were fractionated and the correct boiling point fraction used. The azines were analysed in all cases. Unless otherwise stated the analyses agreed with those required.

ACETOPHENONE AZINE was obtained by treating the ketone (10 g.) with 60% w/w hydrazine hydrate (2 c.c.). Crystals separated on the solution standing overnight. Yield 60% of theoretical.

m-NITROACETOPHENONE AZINE was obtained by treating the ketone (2 g.) dissolved in ethanol with 60% w/w hydrazine hydrate (0.5 c.c.) The solutions were heated on the water bath for 6 hours and crystals separated on the solution being allowed to stand over night. Yield 55% of theoretical.

o-HYDROXYACETOPHENONE AZINE was obtained by refluxing a solution of the ketone (1 g.) in ethanol with 60% w/w hydrazine hydrate (0.5 c.c.) for 5½ hours. Crystals separated on the solution standing for 15 hours. Yield 40% of theoretical.

p-METHOXYACETOPHENONE AZINE was obtained using the method of Boray, Braude and Piaka[20]. The ketone (7.5 g.) was dissolved in ethanol and added to a warm solution of hydrazine sulphate (3.25 g.) and sodium carbonate in water. The azine was recrystallised from benzene. Yield 12% of theoretical.

BENZOPHENONE AZINE was prepared by refluxing the ketone (10 g.) dissolved in 96% ethanol with 96% hydrazine solution (S.G. 1.008) (0.9 c.c.) for 8 hours. Crystals of the azine separated after the solution had been kept at -10°C for 6 weeks. Yield less than 1%. A further preparation involved refluxing the ketone (14 g.) dissolved in chloroform with 96% hydrazine (2 c.c.) for 55 hours. On evaporating off the chloroform layer a golden liquid remained which was used without further purification.

ACETONE KETAZINE, ETHYL-METHYL KETAZINE, DIETHYL KETAZINE, n-di-PROPYL KETAZINE, ACETALDAZINE AND PROPALDAZINE were all prepared by an

analogous method to that quoted in Beilstein[19] viz: 60% hydrazine hydrate was cooled in a salt/ice mixture and the ketone or aldehyde added slowly (2 mols. of the aldehyde/ketone to 1 mol. of hydrazine -- about 30 g. of the ketone was taken in each case, the temperature never being allowed to exceed 10°C. Potassium carbonate was added until the solution became pasty and the mixture allowed to stand for some days. The ketazine was then ether extracted and the ether distilled off. The correct boiling fraction was used. Yields were of the order of 50%. In the case of acetone ketazine the fraction required, that distilling over between 131°C and 132°C gave a low hydrazine analysis, 26.9% compared with a theoretical figure of 28.6%. The refractive index at 25°C was found to be 1.446, required 1.45. Moisture (tested for with anhydrous copper sulphate) was absent. The reason for the low value could not be explained. (It might be due to some ketone being present which seems most unlikely).

CYCLOHEXANONE AZINE; preparation of this compound was attempted by treating the ketone (6.5 g.) dissolved in anhydrous ether with 96% hydrazine (1.11 g.). After standing for 12 hours a yellow oil separated which decomposed when attempts were made to ascertain its boiling point.

ACETONE HYDRAZONE was prepared by the method of Curtius and Pflug[22] viz: acetone (15 g.) was added gradually to a mixture of 60% w/w hydrazine hydrate (15 g.) and barium oxide. After seven days the impure base was ether extracted and distilled.

CHLORO- AND BROMOPLATINIC ACIDS were prepared during the preliminary

stages of the work by dissolving platinum metal in aqua regia, evaporating almost to dryness and then doing repeated evaporations (7-8 in all) with either concentrated hydrochloric acid or with a bromine/hydrobromic acid mixture. In the latter stages of the work, pure platinic chloride and platinic bromide were used as starting materials. They were dissolved in either hydrochloric or hydrobromic acid, evaporated to dryness and then taken up in the solvent being used.

GALLIUM METAL used was either spectrographically pure metal available in the department or pure metal obtained from reputable suppliers.

GALLIUM HYDROXIDE (hydrated gallium oxide ?) was either obtained from gallium residues or from gallium sesquioxide. In the first instance, the residues were acidified to methyl violet and any group two impurities precipitated. Germanium which was present was removed by distillation from concentrated HCl and the hydroxide was then precipitated by making the resultant solution just alkaline to methyl red indicator with ammonia solution (S.G. 0.88). In the latter case the oxide was dissolved in 40-50% hydrofluoric acid and the hydroxide precipated by making the solution just alkaline to methyl red indicator using 0.88 ammonium hydroxide.

GALLIUM TRIFLUORIDE TRIHYDRATE was prepared by dissolving gallium hydroxide in 40-50% hydrofluoric acid, or by dissolving gallium metal in aqua regia, evaporating almost to dryness and then doing three evaporations to dryness with 40-50% hydrofluoric acid.

GALLIUM CHLORIDE, GALLIUM BROMIDE AND GALLIUM IODIDE were not isolated. In all cases gallium metal was dissolved in aqua regia, taken almost to dryness and then evaporated almost to dryness three times with A.R. concentrated hydrochloric acid, A.R. bromic acid/bromine mixture, or A.R. iodic acid respectively. The products, after the third evaporation, were taken almost to dryness and the resulting syrups used.

INDIUM METAL was obtained from reputable suppliers.

INDIUM FLUORIDE, INDIUM CHLORIDE, INDIUM BROMIDE AND INDIUM IODIDE were obtained by analogous methods to those used for the gallium halides.

(3) Analytical Methods.

HYDRAZINE was determined by the direct iodate titration (Andrews's) method[23,24,25,26], aldehyde or ketone being removed as a preliminary to analysis by boiling with 5N hydrochloric acid.

CARBON AND HYDROGEN were determined in the conventional combustion train.

KETONES were determined by the hypoiodate (Messinger's) method[27,28,29].

PLATINUM was determined gravimetrically by combustion to the metal.

HALOGENS (with the exception of fluorides) were determined by Volhard's method. It is well known that solutions of chloroplatinates do not yield pure silver chloride on treatment with silver salt solutions and therefore Volhard's method would not give the true chloride content. During preliminary work on the chloroplatinate of dimethyl ketazine it was noted that the solution in water decomposed on boiling (due to the presence of hydrazine) with the formation of platinum black. This suggested the use of hydrazine as a means of destroying the complex anion prior to the estimation of halogen with silver nitrate. The method employed was to dissolve the salt in water, if necessary, with the aid of halogen free sodium hydroxide, boil and then add an excess of 3% hydrazine hydrate solution. The solution was then boiled to coagulate the platinum. On occasion a few milliliters of sodium hydroxide were needed to complete the destruction of the anion. The

excess of 3% hydrazine hydrate solution (approx. 5 c.c. for 0.2 gm. samples) added. The solution was then made alkaline with halogen free sodium hydroxide and boiled for a few minutes in order to coagulate the platinum which had precipitated. The platinum was filtered off and weighed, if desired, to check with the direct combustion figure. The clear solution was made acid with nitric acid and the halide determined by Volhard's method. This technique was checked using ammonium chloroplatinate and potassium chloroplatinate with the results shown below:

Substance	Chlorine Found	% Calculated
$(NH_4)_2PtCl_6$	48.1	48.0
K_2PtCl_6	43.8	43.8

The method was extended by Pugh[23] to a variety of chloro- and bromo-platinates. In all cases the solution after treatment contained the whole of the originally covalently-bound halogen in ionic form.

FLUORIDE was determined by the lead chlorofluoride method. This method is empirical and precautions have to be taken to avoid excessive solubility losses. Saylor and his co-workers[24] have shown that modifications of the method give results that can be high by as much as 3%; before deciding to use this method therefore a number of methods were considered.

Most of the techniques described recently are for traces of fluoride and were not entertained. Three methods other than the

lead chlorofluoride method were considered:

(i) Gravimetric analysis precipitating the fluoride as calcium fluoride. Solubility of the calcium fluoride is 16 mg/litre as compared with 370 mg/litre for lead chlorofluoride. The disadvantage is that the precipitate is gelatinous and difficult to handle.

(ii) Precipitation as lanthanum fluoride. Here also gelatinous precipitate is obtained. Popov and Wendlandt[25] published a modification to this method while the work described in this thesis was in progress. The modification, even though it eliminated the gelatinous precipitate, was fairly involved, and no change in the method employed was made.

(iii) Titration with thorium nitrate[26]. This method had been used by Pugh and its use was contemplated. The end point of the titration was not very precise however. Determinations of fluoride on pure gallium trifluoride, trihydrate were made using this method and the lead chlorofluoride method. The latter gave far more accurate results and was finally chosen.

Towards the end of the work described in this thesis, a high frequency titration method was published by Dowdall, Sinkinson and Stretch[27]. This method enabled fluoride to be estimated rapidly and was tried on compounds which had been analysed chemically. The method proved

satisfactory when tried with sodium fluoride and hydrazine dihydrofluoride; but gave inaccurate results with the fluorogallates, possibly because of complexing of gallium and fluoride ions in solution.

CHLORIDE, BROMIDE and IODIDE in the simple salts were determined by Volhard's method.

HYDRAZINE was determined by the direct iodate titration (Andrew's) method[28,29,30,31]. Difficulty was found in getting the aromatic compounds into solution, and hydrolysis with 5N sodium hydroxide was sometimes necessary. Aldehyde which interfered with the titration was removed as a preliminary to analysis by boiling with 5N hydrochloric acid. Reduction of the platinum from the platinic to the platinous state occurred on occasion and the titre obtained was greater than that required theoretically. A correction factor (see Page 49) was used for these titrations.

GALLIUM and INDIUM were determined gravimetrically. The salt was evaporated 7-8 times with concentrated nitric acid, heated strongly and weighed as the oxide.

PLATINUM was determined gravimetrically by combustion to the metal.

SULPHATE was determined gravimetrically after precipitation as barium sulphate.

CARBON and HYDROGEN were determined in the conventional combustion train.

KETONES were determined by the hypoiodate (Messinger's) method[32,33,34].

(3) Preparative methods and analytical results.

(i) Halegeno-platinates of the aldazines and ketazines.

1 gm. of hydrazine hydrochloride was dissolved in aqueous acetone (2 c.c. acetone 2 c.c. water). On adding a solution of chloroplatinic acid (equivalent to 1 gm. platinum) in water a precipitate formed. Addition of excess acetone (ultimately 6 c.c. were added) yielded a crop of orange coloured crystals. These were dried under vacuum over concentrated sulphuric acid. Yield 2 gm. Analysis gave N_2H_4 10.5; Pt 31.4; Cl 33.7%. Acetone ketazine chloroplatinate requires N_2H_4 10.1; Pt 30.9; Cl 33.6%. The salt melted at 157-8°C with active decomposition to give gas and sublimate. No blackening was observed.

Bromoplatinic acid (equivalent to 0.25 gm. of platinum) was dissolved in water and treated with excess acetone. To this solution was added a solution prepared by neutralising (to methyl red) 0.4 c.c. of 60% hydrazine hydrate with 50% hydrobromic acid.

After standing at room temperature for a few hours a crop of crystals resulted. These were washed with 1 c.c. water containing 1 drop of hydrobromic acid and 1 drop of ketone. Yield, after drying, 0.2 gm. The mother liquor was left in a desiccator for 48 hours during which time almost all of the liquid evaporated. After standing for 3 days a second crop of crystals was obtained. On being dried their colour changed from red-orange to yellow to grey-black. On being moistened they turned yellow and dissolved.

ANALYSIS.

1st Crop: N_2H_4 18.55%. Acetone ketazine bromoplatinate requires N_2H_4 7.1; Pt 21.7; Br 53.3%.

The crystals were added to the mother liquor and excess acetone added. The acetone was warmed until all the solid had dissolved and the solution allowed to cool. Brick coloured needles came down. These were dried and analysed. Found: N_2H_4 6.8; Br 53.0%.

2nd Crop: Found N_2H_4 7.3; Br 58%. These figures looked promising and the preparation was repeated on a larger scale.

Bromoplatinic acid (equivalent to 1.4 gm. of platinum) was evaporated down to dryness on the water bath and then taken up in acetone. 2.3 c.c. of 60% hydrobromic acid (S.G. 1.7) was added to 6 c.c. of water. 1 c.c. of 60% hydrazine hydrate was then added and the solution evaporated almost to dryness on the water bath. The concentrate was then dissolved in 2-3 c.c. of acetone containing 5 drops of water. The hydrazine hydrobromide solution was added slowly to the bromoplatinic acid solution and a red precipitate formed almost immediately. The product was separated, washed with small quantities of acetone and dried. Yield 4.25 gm. Analysis gave N_2H_4 6.9; Pt 22.9; Br 54.5%. M. pt. 82-84°C.

Attempts to recrystallise the above compound gave a yellow solid, which did not contain hydrazine. (It was insoluble in hydrochloric acid and water, but dissolved in warm ammonium hydroxide solution. On being heated strongly colloidal platinum was precipitated from

the solution. When heated with aqueous sodium hydroxide colloidal platinum was formed. No effect on litmus was noted but a faint smell of ammonia was detected. When the recrystallisation liquor was evaporated almost to dryness a red product was obtained which contained 7.8% hydrazine. The product appeared to be the salt sought, but was somewhat impure.

At a later stage attempts to obtain a purer sample of the salt using acetone ketazine instead of acetone and hydrazine were made. The azine was dissolved in ether (1 c.c. azine in 10 c.c.), cooled to 0°C and treated with bromoplatinic acid (1 gm.) dissolved in n-butyl alcohol. (The reason for using n-butyl alcohol as solvent is discussed below). A red powder precipitated immediately, this was separated washed with ether, dried and analysed. Analysis gave N_2H_4 8.7; Pt 22.9; Br 59%, giving a ratio of N_2H_4:Pt:Br of 2.4:1:6.5; i.e. the compound prepared by this method was less pure than the one previously obtained.

DIETHYL KETAZINE.

Chloroplatinic acid (equivalent to 1 gm. of platinum) dissolved in 5 c.c. of water was treated with 1 gm. of hydrazine dihydrochloride. Violent gas evolution took place and heat was liberated. Colloidal platinum was formed in appreciable amounts.

Approximately 1 c.c. of the ketone was added and the solution cleared. The colloidal platinum was removed and a further 1.5 c.c. of ketone was added. The solution was allowed to cool. A crop of

crystals formed and was separated. These crystals contained colloidal platinum. On the mother liquor being left in the refrigerator overnight a second crop of crystals was obtained. These were separated and the mother liquor was allowed to evaporate slowly, initially at room temperature and then on the water bath. A third crop of product was obtained.

On analysis the first crop gave a negligible hydrazine titre. The second crop contained between 12.7 and 13.7% hydrazine, different samples giving different values. The third sample had 19.6% hydrazine.

The second crop was washed thoroughly with aqueous acetone and dried under vacuum. Analysis gave N_2H_4 13.2; Pt 56; Cl 31.2%. This gave a ratio of N_2H_4 : Pt : Cl :: 1.5 : 1 : 3 or 3 : 2 : 6.

Testing with dinitrophenylhydrazine gave negative results i.e. no ketone present.

The preparation was repeated using hydrazine monohydrochloride instead of hydrazine dihydrochloride, the ketone being added this time at the beginning of the preparation.

1 gm. of platinum as chloroplatinic acid was dissolved in water and 0.5 c.c. of the ketone was added. On adding the ketone the solution became ice cold. This solution and the hydrazine monohydrochloride solution were mixed and a large volume of gas was given off. A yellow powder (A) came down and some colloidal platinum was seen. The solution had become quite warm at this stage.

The powder was separated and a further 0.5 gm. of hydrazine monohydrochloride added. The solution was allowed to stand and crystals separated. The mother liquor was left in the refrigerator for 12 hours and a further crop of product was obtained. These two crops were combined and treated with excess ketone; a change in structure appeared to take place. The resulting crystals (B) were filtered off, washed with ketone and dried under vacuum for 1 hour. On being removed from the desiccator a strong smell of hydrochloric acid gas was noticed. The crystals were stored in a desiccator over sulphuric acid.

On analysis Crop (A) gave N_2H_4 22% and 24.8% on separate samples, and Cl 61%. Crop (B) gave N_2H_4 15.2; Cl 34.1%. [$(N_2H_4)_2PtCl_4$ requires N_2H_4 15.8; Pt 48.8; Cl 35.3%]. The compound was dried for a further 8 hours under vacuum and re-analysed. Found Pt 44.3; Cl 33.2%.

The hydrazine titrations were done with some difficulty as the pink coloration in the carbon tetrachloride layer (colourless at end point) kept on returning. Ultimately after adding small quantities of iodate over a period of hours no pink coloration returned after 45 minutes. Initially N_2H_4 was found to be 16.9%, on the second and more slowly done titration 17.7% of hydrazine was found to be present.

During the titration with iodate the following reactions are possible:

$$Pt^{2+} \rightarrow Pt^{4+} + 2e$$

$$N_2H_4 \rightarrow N_2 + 4H^{+} + 4e$$

As two mols. of hydrazine were present, eight electrons would have been involved in the oxidation, i.e. a total of ten electrons were transferred. Assuming that 4/5 of the titre was due to the hydrazine, the hydrazine percentage was recalculated to be 14.2%. Taking 1/5 of the titre as being due to the platinum, the platinum percentage was determined and found to be 44.1%. This agreed with the 44.3% found by direct combustion.

The chloride was then re-determined using a modified Volhard titration with nitrobenzene used to coagulate the precipitate. Chloride was found to be 34%.

The mother liquor was left in the deep freeze (-10°C) for three weeks and a very small crop of crystals (0.36 gm.) was obtained. On analysis these gave: N_2H_4 13.7; Pt 33.4; Cl 35.6%. The hydrazine titration was again very slow.

At this stage it was decided to repeat the preparation keeping the solutions at 0°C.

Chloroplatinic acid (equivalent to 1 gm. platinum) was dissolved in 5 c.c. of water and 1 c.c. of the ketone added. The solution was warmed for a few minutes and then cooled in melting ice.

0.8 gm. of hydrazine monohydrochloride was dissolved in 1 c.c. of water and 1 c.c. of the ketone added. This mixture was boiled for a few minutes, allowed to cool to room temperature and then cooled to 0°C. When both solutions had cooled to 0°C, the hydrazine hydrochloride

solution was added to the chloroplatinate solution. Small quantities were added at a time, the solution being cooled between additions. The ketone layer became brown in colour after the first addition and successive additions caused vigorous gas evolution. When all the hydrazine hydrochloride solution had been added the mixture was shaken thoroughly and placed in the deep freeze. After 2-3 hours the upper ketone layer contained a greyish precipitate and a few crystals had appeared in the lower layer.

After being left in the deep freeze overnight, the ketone layer had become black in colour and there was an appreciable quantity of crystals in the lower layer. The solutions were allowed to stand at room temperature and the ketone layer separated. The liquor of the bottom (aqueous) layer was decanted, and on standing a second crop of crystals appeared.

The first crop of crystals contained some colloidal platinum. These were dried in air and analysed. The hydrazine titrations were again slow and different samples gave respectively 15.9, 15.4 and 14.2% N_2H_4; Pt. on combustion was 44.9%, taking one fifth of the lowest hydrazine titre gave 43.4%. Cl was found to be 35.5%. Taking the highest platinum and hydrazine values, we get a total of 96% and a ratio N_2H_4 : Pt : Cl of 2.1 : 1 : 4.4.

The second crop was analysed and gave N_2H_4 14; Pt 39.4 (titration), 48.2 (combustion); Cl 39.2-44%.

At this stage of the work it was thought that better results

might be obtained if bromoplatinic acid were used instead of chloroplatinic acid. On the one hand,a larger molecular weight would reduce slight variations in the calculated percentages required, and on the other, bromide could be determined more easily and accurately than chloride by the Volhard's titration.

Bromoplatinic acid (equivalent to 2 gm. of platinum) dissolved in 50% hydrobromic acid was cooled in melting ice and treated with 2.5 c.c. of the ketone.

0.8 c.c. of 60% hydrazine hydrate was acidified (to methyl red) with hydrobromic acid and was then treated with 2.5 c.c. of the ketone. The indicator turned yellow during the addition. The resulting solution was cooled in melting ice.

The solutions were mixed slowly, the temperature being kept at 0°C. A brick red product precipitated almost immediately. This was separated, washed with ether and dried. Yield 4.95 gm. The product dissolved readily in water with some gas evolution and slight reduction. Positive results were obtained on testing for the presence of ketone with 2.4.dinitro-phenyl hydrazine. On being heated the amorphous product blackened at 135° and decomposed at 170°. Analysis gave N_2H_4 6.4; Pt 21.7; Br 56%. The bromoplatinate of the hydrazone of diethyl ketone requires N_2H_4 7.3; Pt 22.2; Br 54.7%.

As what appeared to be the bromoplatinate of the hydrazone had been prepared, a further attempt was made to prepare the chloroplatinate. This time water was eliminated as far as possible.

Chloroplatinic acid (equivalent to 1 gm. of platinum) was evaporated to dryness and then taken up in 16 drops of concentrated hydrochloric acid. The solution was cooled in melting ice and when cold 1.2 c.c. of diethyl ketone added. The solution was kept at 0°C.

0.6 c.c. of 60% hydrazine hydrate was made acid (to methyl red) with concentrated hydrochloric acid, cooled in melting ice and 1.2 c.c. of diethyl ketone added.

The hydrazine hydrochloride solution was added to the platinum solution, the mixture being kept at 0°C. When approximately half the hydrazine solution had been added, vigorous gas evolution took place and when approximately three-quarters of the solution had been added an orange precipitate began to separate. Precipitation was complete a few minutes after all the solution had been added. The precipitate was filtered off, washed with 1 c.c. of the ketone, dried between filter papers and then sun-dried for 30 minutes. The yield was 0.95 gm.; a second crop (yield 0.4 gm.) came down subsequently. The salt gave a positive reaction with d.n.p. reagent and dissolved in water with vigorous gas evolution. On heating it darkened at 120°C and melted at 187-188°. Analysis gave N_2H_4 10.4; Pt 34.5; Cl 34.8%. The chloroplatinate of the hydrazone of diethyl ketone required N_2H_4 10.5; Pt 32.1; Cl 35.1%. The high platinum value found could be due to traces of colloidal platinum being present. This would also explain the other analyses giving slightly low results.

ETHYLMETHYL KETAZINE.

Preparation of the bromoplatinate was attempted first. 1.3 gm. of the ketone was added to 1 c.c. of 60% hydrazine hydrate and the mixture cooled to 0°C. Bromoplatinic acid (equal to 2 gm. of platinum) was evaporated to dryness and dissolved in 7 c.c. of the ketone containing 5 drops of 50% hydrobromic acid. This solution was also cooled to 0°C.

The solutions were mixed, and the ketone allowed to evaporate slowly. After 24 hours an oil had separated. Over a period of a few weeks a number of crops of solid material were obtained. Crop 1 (yield 0.25 gm.) and Crop 2 (yield 0.89 gm.) both gave on analysis N_2H_4 4.64; Pt 29.4; Br 42.6%. These added up to 76.6% and gave a ratio of N_2H_4 : Pt : Br as 1 : 1 : 3.2. The difference was assumed to be H_2O (equivalent to 8.6 mols.).

The third crop (yield 1.3 gm.) gave a different analysis viz. N_2H_4 9; Pt 36; Br 51.8%. These gave a total of 96.8% and the ratio N_2H_4 : Pt : Br as 3 : 2 : 7. The difference could have been two mols. of water. This appeared to be a covalent compound, (cf. discussion below), but definitely was not the salt sought.

An attempt to make the chloroplatinate by treating 1 c.c. of the already characterised azine with 1 gm. of chloroplatinic acid in anhydrous ether also proved unsuccessful. A yellow oil separated which was dried under vacuum and on analysis appeared to be unchanged chloroplatinic acid. On repeating this preparation a brown-red

amorphous product was obtained which decomposed in the temperature range 181-186°C. All attempts at recrystallisation led to reduction of the product and the formation of colloidal platinum.

At a later stage in the work a further attempt was made to prepare the bromoplatinate using the ketazine in the presence of excess ketone and n-butyl alcohol as solvent.

2 c.c. of the ketazine and 5 c.c. of the ketone were dissolved in 20 c.c. of ether and were cooled to 0°C. 1 gm. of bromoplatinic acid in n-butyl alcohol was added. There was immediate formation of what appeared to be a fine orange precipitate (which could not be filtered) and also a viscous red oily layer which settled to the bottom of the dish. On standing overnight the ether evaporated leaving a clear orange coloured solution. The "precipitate" in all probability had been an emulsion. Adding ether did not reproduce the emulsion. The orange solution left in the deep freeze for some weeks did not yield any solid product. The preparation was repeated with similar results except that formation of the emulsion was obvious. The solution was mixed with that from the previous preparation and both heated on the water bath. A viscous oil resulted which did not solidify even on prolonged standing.

Di-n-PROPYL KETAZINE.

0.3 c.c. of 95% hydrazine and 2.66 c.c. of ethyl methyl ketone were dissolved in absolute ethanol. A solution of bromoplatinic acid (equivalent to 1 gm. platinum) dissolved in absolute ethanol was

added. Vigorous effervescence took place even though the solutions were kept at 0°C, and colloidal platinum came down which was removed.

On standing overnight a yellow powder intimately mixed with colloidal platinum was obtained. On slow evaporation of the solvent a viscous oil resulted, which dried to give a "scaly" product. Water was added and some gas evolution took place with the formation of a red-orange solution. A few c.c. of ethanol were added and the solution heated on the water bath and then allowed to stand at room temperature.

After standing for 5 weeks a few crystals made their appearance, but the crop did not increase during the course of a further 2 weeks. The solution was finally taken to dryness under vacuum in the presence of concentrated sulphuric acid.

On opening the desiccator fumes of HBr were noticed. A small yield (0.09 gm.) of mauve crystals were obtained which deliquesced on being exposed to the air.

A few crystals were dissolved in water. This solution deposited a large amount of colloidal platinum on being reduced with hydrazine in the presence of sodium hydroxide. An appreciable quantity of red precipitate, showing the presence of bromoplatinate, was obtained on treating the solution with silver nitrate in the presence of nitric acid. Negative results were obtained on treating the solution with benzaldehyde or iodate solution and Lassaignes test showed the absence of nitrogen. Hydrazine therefore was not present.

On heating no charring or other indication of organic constituents was noted, and testing with dinitro phenyl hydrazine reagent showed the absence of ketone. Analysis gave Pt 25.9, Br 53%. The melting point was determined as 55-56°C. $H_2PtBr_6.6H_2O$ requires Pt 23.3, Br 57.3% and melts below 100°C.

Further attempts to prepare the salt were made by dissolving 0.35 c.c. of the ketone in 10 c.c. of ether and adding 0.63 c.c. of 60% w/w hydrazine hydrate. When 40% hydrobromic acid was added to acidify the solution hydrazine hydrobromide precipitated.

Adding bromoplatinic acid to the ketone/hydrazine solution led to reduction with the formation of colloidal platinum.

Attempts to make the chloroplatinate by dissolving 1 - 2 c.c. of n-propyl ketazine in anhydrous ether and then adding 1 gm. of chloroplatinic acid in 5 c.c. of ether (containing a few drops of concentrated hydrochloric acid) also proved unsuccessful; even when the solutions were kept at 0°C. The only product isolated was hydrazine hydrochloride contaminated to a greater or lesser extent with chloroplatinic acid.

OTHER ALIPHATIC KETAZINES.

Attempts to prepare complex chloro- or bromoplatinates from methyl-n-propyl ketazine; methyl-iso-propyl ketazine and methyl-di-iso-propyl ketazine proved unsuccessful. In all cases reduction took place after the addition of a few drops of the acid solution.

BENZALAZINE.

Bromoplatinic acid (equivalent to 0.5 gm. of platinum) was dissolved in absolute ethanol and the solution treated with 0.7 c.c. of 60% hydrazine hydrate dissolved in an excess of benzaldehyde. A red-orange product separated which was filtered off, washed with ether and allowed to dry. Yield 0.8 gm. Melting point 188-190°C.

Analysis, gave N_2H_4 5.6; Pt 16.4; Br 48.1%. Benzalazine bromoplatinate requires N_2H_4 5.9; Pt 19.9; Br 43.8%.

The preparation was repeated using as starting materials bromoplatinic acid (equivalent to 0.5 gm. platinum) in absolute ethanol and 1 gm. of benzalazine dissolved in absolute ethanol.

A red-orange product was obtained which was washed with absolute ethanol and dried. Yield 1 gm. A second crop (0.4 gm.) was obtained on evaporating the mother liquor. Analysis gave N_2H_4 5.9; Pt 18.3; Br 44.1%. These crystals melted at 187-189°C.

ACETOPHENONE AZINE.

1 gm. of acetophenoneazine was dissolved in 30 c.c. of warm benzene. Bromoplatinic acid (equivalent to 0.5 gm. platinum) dissolved in 30 c.c. of 50% hydrobromic acid was added.

A yellow-brown product was obtained which was washed with ether, dried between filter papers and left under vacuum overnight.

On examination through the magnifying glass the product was seen

to contain small particles of colloidal platinum. As much of the platinum as possible was removed by hand, and the remainder of the powder was mixed very thoroughly.

The powder which was not very soluble in water, decomposed in hot acid depositing colloidal platinum. It gave positive results on being treated with dinitro phenyl hydrazine reagent and melted sharply at 178-180°C.

Analysis gave N_2H_4 3.6; Pt 11.2; Br 38.8% which gives the ratio N_2H_4 : Pt : Br :: 2 : 1 : 8.6. The total percentage, however, was short of 100% even when allowance for ketone content had been made. It seemed likely that the difference was water. Heating 0.1 gm. for 1 hour at 110-115°C resulted in a 35.7% loss in weight. Reanalysing gave Br 34%, i.e. bromine had also been lost during the heating. N_2H_4 and Pt were re-determined and found to be 6.1 and 16.1% respectively.

Acetophenoneazine bromoplatinate required N_2H_4 5.6; Pt 17; Br 41.8%, and it seemed that this might be the correct salt, but very impure. 0.5 gm. of platinum as bromoplatinic acid was dissolved in absolute ethanol and added to 1.8 gm. of the azine dissolved in "Analar" benzene. A small quantity of solid separated during the addition, but no appreciable increase was noted on leaving the solution standing overnight. The bottom layer had become very viscous.

The solution was evaporated almost to dryness on the water bath, a few drops of hydrobromic acid added and the solution left standing for a few days.

A dark brown (tinged with orange) solid resulted. This was filtered off, washed six times with benzene, four times with ethanol (in which it was slightly soluble) and finally five times with ether. The product was dried between filter papers and left under vacuum for 48 hours.

On heating it melted to give a tarry product and then gave off pungent white fumes (very similar in character to those obtained when heating the product obtained in the previous preparation). Platinum was found to be 26.9%.

Hydrazine and bromine could not be determined as the substance was almost insoluble. Refluxing with a 1:1 concentrated hydrochloric acid-water mixture for four hours did not decompose the product. The preparation was repeated, once again in the presence of aqueous hydrobromic acid.

1.8 gm. of the azine was dissolved in 50 c.c. of benzene. 2 c.c. of 40% hydrobromic acid in 10 c.c. of water and 0.5 gm. of platinum (as bromoplatinic acid) in ethyl alcohol were added and the mixture heated on the water bath. On heating a viscous product formed which settled to the bottom of the dish. The supernatant liquid was decanted into another evaporating basin and both solutions allowed to stand.

A mixture of yellow crystals, brown crystals and a brown oil resulted from the viscous product. The yellow crystals proved to be unchanged azine (contaminated to some extent) while the brown product and the oil did not give consistent repetative analyses.

At this stage it was decided to repeat the preparation by the original method, namely, in the presence of a large quantity of aqueous hydrobromic acid.

1 gm. of the azine was dissolved in 30 c.c. of benzene. 0.5 gm. of platinum as bromoplatinic acid was dissolved in 30 c.c. of 40% hydrobromic acid. This solution which appeared to contain some colloidal platinum was filtered and then added to the benzene solution. A yellow-brown product was obtained which was separated, washed three times with benzene, once with 40% hydrobromic acid and three times with water. It was then dried between filter papers and left under vacuum in the presence of concentrated sulphuric acid for 48 hours.

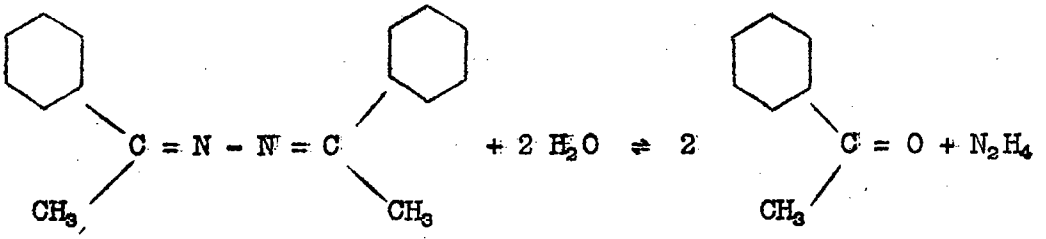
Yield 0.15 gm. Melting point 169-171°C. Platinum content 12.14%. The compound was heated at 100-110°C for 4½ hours and a loss of weight of 27.5% occurred. There were no obvious signs of decomposition, the colour, however, changed to a dark brown. The new melting point was found to be 138-140°C and the bromine content only 16.3%. This product obviously was not the salt sought.

The preparation was repeated with 0.6 gm. of azine in 10 c.c. of benzene. 20 c.c. of 40% hydrobromic acid was added and the mixture

treated with 1 gm. of bromoplatinic acid in 20 c.c. of water. There was no apparent reaction and on evaporation an oil formed which would not solidify.

At this stage it was thought that if a solvent could be found for the bromoplatinic acid which would not decompose the azine, a purer product might result. As the acid dissolved in ethanol, higher alcohols were tried. n-Butyl alcohol proved a suitable solvent.

It was also decided to use the ketone as solvent for the azine in order to further reduce the chance of decomposing the azine. The equilibrium



would tend to be kept to the left if water were reduced to the minimum and acetophenone present in excess.

0.6 gm. of the azine was dissolved in 35 c.c. of acetophenone. 1 gm. of bromoplatinic acid (made by treating platinic bromide with hydrobromic acid and then evaporating to dryness) was dissolved in 35 c.c. of n-butyl alcohol.

The acetophenone solution was placed in melting ice and set solid. (Acetophenone melts at 19.7°C). It was allowed to thaw and the bromoplatinic acid solution was stirred in. The two solutions were

perfectly miscible and there was no apparent reaction.

The mixture was left standing overnight and a red solid separated which was filtered off, washed four times with ether and dried under vacuum in the presence of concentrated sulphuric acid. Yield 0.42 gm. Melting point 190-191°C. Analysis gave N_2H_4 5.6; Pt 17.1; Br 42.5%. Acetophenoneazine-bromoplatinate required N_2H_4 5.7; Pt 17.3; Br 42.5%.

Attempts to make the chloroplatinate proved unsuccessful, the only product which could be isolated was impure hydrazine dihydrochloride. This was probably the least soluble of all the products present in solution.

BENZOPHENONE AZINE.

1 gm. of benzophenone was dissolved in 80 c.c. of chloroform. 0.7 gm. of the benzophenoneazine hydrochloride previously prepared was added, but did not dissolve to any appreciable extent. 15 c.c. of nitrobenzene and 5 c.c. of n-butyl alcohol were added and the mixture heated on the water bath for one hour. During this period most of the azine dissolved. The hot solution was filtered as rapidly as possible and 1 gm. of chloroplatinic acid, dissolved in ether added. After standing for three hours a yellow oil separated which gave a small yield of white powder on being left overnight. The powder proved to be hydrazine hydrochloride. The filtrate was left in the deep freeze for 10 days, but no further solid product precipitated. It was then heated on the water bath and a viscous oil was obtained which

could not be induced to solidify.

An attempt was subsequently made to prepare the bromoplatinate. 5 gm. of benzophenone was dissolved in 60 c.c. of chloroform and 0.5 c.c. of 95% hydrazine added. The mixture was heated under reflux for 1 hour, and a cloudy solution resulted. This was allowed to stand for 12 hours and then cooled to 0°C, no solid product separated. 1 gm. of bromoplatinic acid dissolved in n-butanol was then added. The solution became more milky and then developed a brown (milky coffee) colour. A few drops of hydrobromic acid were added and a yellow powder, which proved to be hydrazine dihydrobromide contaminated with bromoplatinic acid, separated.

ACETALDAZINE.

2 c.c. of acetaldazine and 5 c.c. of acetaldehyde were dissolved in 20 c.c. of ether and the solution cooled to 0°C. 1 gm. of bromoplatinic acid dissolved in 5 c.c. of n-butyl alcohol was added. Immediate precipitation of an orange powder took place.

The powder was filtered, washed five times with ether and left under vacuum over concentrated sulphuric acid overnight. Yield 0.8 gm. Analysis gave Pt 19.0; Br 45.4%.

Iodate gave an immediate titre equivalent to 3.03% of hydrazine, i.e. 1 mol. The pink colour in the carbon tetrachloride layer came back slowly, and small additions of iodate brought the value up to 5.1%. Repeating the hydrazine determination, after ensuring that all

the aldehyde had been removed by boiling with concentrated hydrochloric acid gave an immediate titre equivalent to 3.05%. Additional amounts of iodate were added until no pink coloration returned after 24 hours. This titre was again assumed to be both hydrazine and platinum. 4/5ths of the titre gave N_2H_4 6.3% and 1/5th gave Pt 19%. This latter figure agreed with the value found by combustion.

A combustion analysis for carbon and hydrogen gave the following C 18.1; H 3.3%. The total percentage did not add up to 100%, the difference, however, might be explained by the presence of oxygen.

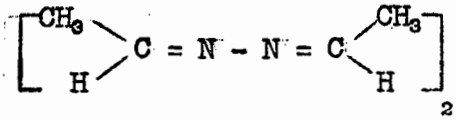
The preparation was repeated as follows. 2 c.c. of acetaldazine and 5 c.c. of acetaldehyde were dissolved in 20 c.c. of ether, and cooled to 0°C. 1 gm. of bromoplatinic acid in 10 c.c. of n-butanol was added slowly. There was immediate precipitation of an orange powder. Yield 0.9 gm. M. pt. 106-107°C.

The hydrazine determination, as before, was done with some difficulty. Half the final figure was obtained almost immediately, the remainder of the hydrazine reacting very slowly. The final addition of iodate was made some 24 hours after the titration was commenced.

On heating a solution of the compound to $\pm$ 80°C the titration took only a few minutes and a hydrazine value of 6.0% was obtained. (A possible explanation for the slow titration is given below).

Analysing for the other elements present gave the following results:

Pt 18.5; Br 45.4; C 19.8; H 3.5%. These give the following ratio. N_2H_4 : Pt : Br : C : H : :: 1.98 : 1 : 6 : 17.4 : 36.5, i.e. there are either four or five extra acetaldehyde molecules present.



$PtBr_6$ $5CH_3CHO$ requires N_2H_4 6.0;
Pt 18.3; Br 45; C 14.6; H 3.6%.

With the exception of the carbon these figures agreed with those determined experimentally. No explanation for the low carbon figure could be found.

Attempts to make other salts of acetaldazine had shown them to be decomposed by the smallest traces of water or of free acid. To see whether acetaldazine would give a bromoplatinate under aqueous/acid conditions, the preparation was repeated as follows.

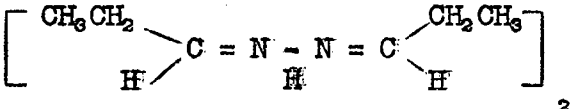
1 c.c. of acetaldazine and 2.5 c.c. of acetaldehyde were dissolved in 10 c.c. of ether and cooled to 0°C. 0.5 gm. of bromoplatinic acid were dissolved in 10 c.c. of 50% hydrobromic acid. The solutions were mixed and two immiscible layers formed. The addition of 10 c.c. of absolute ethanol, however, resulted in a homogeneous solution. On standing for 72 hours a few red crystals made their appearance. The crop did not increase on standing for seven days. Attempts to concentrate the solution were unsuccessful. Heating the solution led to decomposition with the formation of colloidal platinum.

PROPIONALDAZINE.

5 c.c. of propionaldehyde in 20 c.c. of ether was treated with 0.5 c.c. of 64% hydrazine hydrate. On adding the hydrazine solution a vigorous reaction took place. The mixed solutions were cooled to 0°C and 1 gm. of bromoplatinic acid in n-butyl alcohol was added. There was immediate precipitation of an orange powder. This was filtered off, washed four times with ether and dried in air. Yield 0.9 gm. M. pt. 78-79°C.

In the cold the hydrazine solution was again very slow, warming the solution to 80°C enabled the titration to be completed within a few minutes.

Analysis gave the following results: N_2H_4 6.0; Pt 18.7; Br 45.0; C 21.4; H 3.7%. This gives the ratio N_2H_4 : Pt : Br : C : H :: 2 : 1 : 6 : 18 : 38, i.e. there appear to be two aldehyde molecules more than expected.



$PtBr_6 . 2CH_3CH_2CHO$ requires

N_2H_4 6.3; Pt 19.2; Br 47.3;

C 21.3; H 3.7%.

Infra-red spectra were taken of these compounds which showed that the extra aldehyde molecules were not present as free aldehyde. The results of the infra-red analyses are discussed below.

n-BUTYRALDAZINE.

0.4 c.c. of n-butyraldehyde was dissolved in 10 c.c. of ether and treated with 0.12 c.c. of 64% hydrazine hydrate. The mixture was cooled to 0°C and bromoplatinic acid added. Reduction took place with the formation of colloidal platinum.

The preparation was repeated using an excess of the aldehyde. 0.8 c.c. of hydrazine hydrate was added to 5 c.c. of the aldehyde dissolved in 10 c.c. of ether. 1 gm. of bromoplatinic acid, dissolved in n-butanol, was added. There was no apparent reaction. No product was obtained on prolonged standing. Heating the solution led to decomposition.

MIXED AZINE FROM ACETOPHENONE AND BENZALDEHYDE.

The simple salts of mixed bases had been made by treating a mixture of the azine of the aldehyde and excess ketone with halogen acid. The "mixed base" salt being the least soluble had separated from the equilibrium mixture (see below).

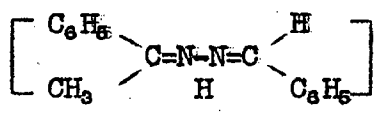
As the bromoplatinates of acetophenoneazine and benzalazine had similar melting points, 190-191°C and 187-189°C respectively, and as their analyses did not differ appreciably it was decided to make the hydrazone of acetophenone and then to treat this with benzaldehyde and bromoplatinic acid rather than use an equilibrium mixture.

The hydrazone was made (cf. J.C.S. Abstracts, 1935, pg. 1891) by digesting a mixture of acetophenone (10 gm.) with hydrazine hydrate

(8 gm.) and some sticks of barium oxide for three days on the water bath. More barium oxide was added and then five volumes of ether. The suspension was filtered and the filtrate fractionated.

The 240-260°C fraction was taken and treated with 10 gm. of benzaldehyde and 2 c.c. of chloride free 2 N sodium hydroxide (cf. J.C.S. Abstracts 1892, Part I, pg. 451). A yellow oil resulted, colloidally dispersed. 15 c.c. of this colloidal dispersion was taken, cooled in melting ice, and treated with a solution of 0.5 gm. of bromoplatinic acid dissolved in n-butyl alcohol. After 1 - 2 minutes an oil started to separate and 5 c.c. of 50% hydrobromic acid was added. After an hour an appreciable quantity of oil was present.

The oil was left in contact with the mother liquor overnight and a crop of red crystals were obtained. The crystals were separated, washed three time with ether and dried in the sun. Yield 0.31 gm. M. Pt. 214-216°C. Analysis gave N_2H_4 5.0; 15.1; Br 37.4%.



Pt Br_6 required N_2H_4 5.0; Pt 15.2; Br 37.4%

{ Benzalazine bromoplatinate

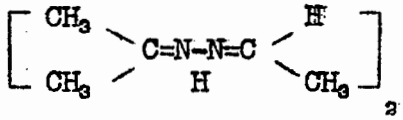
M. Pt. 187-189°C. N_2H_4 5.9; Pt 17.9; Br 43.8%

Acetophenoneazine bromoplatinate

M. Pt. 190-191°C. N_2H_4 5.6; Pt 17.0; Br 41.8%. }

Mixed azine from Acetone and Acetaldehyde.

4 c.c. of acetaldazine and 2.5 c.c. of acetone were dissolved in 20 c.c. of ether. After being cooled to 0°C, 1 gm. of bromoplatinic acid dissolved in n-butanol was added. There was immediate precipitation of a red-orange product. The product was separated, washed four times with ether and dried in air. Yield 0.8 gm. M. Pt. 94-96°C. Analysis gave N_2H_4 6.3 (⅓ of titre); Pt 19 (⅔ of titre), 18.8 (combustion); Br 41.8%.



$_2$ $PtBr_6$, required N_2H_4 6.2; Pt 18.9; Br 46.4%

The bromine figure was very low. The preparation was repeated, this time using acetone ketazine and acetaldehyde as starting materials.

2 c.c. of acetone ketazine and 1 c.c. of acetaldehyde were dissolved in 10 c.c. of ether and cooled to 0°C. 1 gm. of bromoplatinic acid in n-butyl alcohol was added. A red oil separated immediately. The mother liquor was decanted and the oil washed three times with 10 c.c. lots of ether and left under vacuum for 24 hours. It was then allowed to stand at room temperature. All attempts to induce crystallisation over the course of two months proved unsuccessful.

Mixed azine from Acetone and Benzaldehyde.

1.2 gm. of benzalazine and 2 c.c. of acetone were dissolved in 20 c.c. of ether and the mixture cooled in melting ice. 0.5 gm. of

bromoplatinic acid in n-butanol was added. There was immediate precipitation of orange product. On standing for a few minutes a second, colourless, gelatinous precipitate made its appearance. The precipitate dissolved on the addition of ether. The orange precipitate was filtered off, washed six times with 15 c.c. portions of ether and dried under vacuum.

Analysis gave N_2H_4 9.7; Pt 8.8; Br 23.1%. This gives a ratio of N_2H_4 : Pt: Br as 6.8: 1 : 6.4. The bromoplatinate of the mixed azine required N_2H_4 6.4; Pt 19.6; Br 48.2%.

Attempts to purify this compound led to decomposition. The product was probably a mixture of more than one azine salt.

Mixed azine from Acetaldehyde and Acetophenone.

2 c.c. of acetaldazine and 1 c.c. of acetophenone were dissolved in 20 c.c. of ether, cooled to 0°C and treated with 0.5 gm. of bromoplatinic acid dissolved in n-butyl alcohol.

The solution became cloudy and an orange oil separated. On standing needles formed which were washed with water (four times), acetone (twice) and ether (twice). The crystals melted at 121-122°C and on analysis proved to be acetophenone azine, i.e. of all the possible products the acetophenoneazine is the least soluble.

Mixed azine from Acetaldehyde and Benzaldehyde.

2 c.c. of acetaldazine and 1 c.c. of benzaldehyde were dissolved in 10 c.c. of ether and cooled in melting ice. On being treated with

a solution of 0.5 gm. of bromoplatinic acid dissolved in n-butanol, a viscous red oil separated. No solidification occurred on standing for five days. The oil was then heated on the water bath. A solid mass formed which did not give repetitive analyses.

Mixed azine from Acetophenone and Acetone.

1 gm. acetophenoneazine was dissolved in a mixture of 30 c.c. acetophenone and 30 c.c. acetone. The mixture was cooled to 0°C and treated with 0.5 gm. of bromoplatinic acid dissolved in n-butyl alcohol. A clear liquid resulted which did not yield a product even on prolonged standing. When heated on the water bath a viscous oil separated which could not be induced to solidify.

Attempts to make simple salts from acetophenoneazine-acetone mixtures had proved unsuccessful (see above), and attempts to prepare the free base from the hydrazine of acetone and acetophenone yielded acetophenoneazine.

Pyrazoline.

Attempts to make simple salts of aliphatic ketazines had lead to ring closure in some instances (see above). The ring closed products, however, had not yielded salts with chloroplatinic acid.

Pyrazoline was prepared and treated with the halogeno platinic acids and salts were obtained. Details of these preparations are not given as the results of a fuller investigation of the salt forming

properties of the 3 : 5 : 5-trimethyl-Δ^2-pyrazolinium ion and of the 3 : 5 : 5-trimethyl-1-isopropylidene-Δ^2-pyrazolinium ion undertaken by the late Professor W. Pugh have already been published[37].

Condensation products of aldehydes and ketones with salts of some substituted Δ^2-pyrazolines and hydrazines were subsequently investigated by Lamchen, Pugh and Stephen. The results of this research have also been published[38].

(ii) Simple salts of ketazines.

ACETOPHENONE AZINE.

0.5 gm. of the azine was dissolved in dry ether and dry hydrochloric acid gas was passed through the solution for 5-10 minutes. A white crystalline solid separated. This was washed with ether and dried. M. pt. 132-134°C. Analysis gave N_2H_4 11.8; Cl 13.4%. NN' di (1-phenyl ethylidene) - hydrazinium chloride (methyl phenyl ketazine hydrochloride) requires N_2H_4 11.7; Cl 13.0%. The salt hydrolyses easily and fumes in air.

0.44 g. of the azine was dissolved in ether and treated with a stoichiometric quantity of 98% sulphuric acid in ether. A white crystalline solid separated, which was washed with ether and dried over sulphuric acid. M. pt. 125-126°C.

Analysis gave N_2H_4 9.8; SO_4 29.4%. NN' di (1 phenyl ethylidene)-hydrazinium hydrogen sulphate (methyl phenyl ketazine hydrogen sulphate) requires N_2H_4 9.6; SO_4 28.8%.

m-NITRO ACETOPHENONE AZINE.

Approx. 0.3 g. of the azine was dissolved in a suitable solvent, warm xylol, and dry hydrochloric acid gas passed through the solution for 5-10 minutes. The solution became cloudy initially, but cleared as the gas bubbled through. On standing no product precipitated. This might have been due to insufficient hydrochloric acid gas being dissolved in the xylol. The procedure was repeated using nitrobenzene as solvent. Here again no product was obtained.

The hydrochloric acid gas was boiled off and a few cubic centimetres of 48% hydrobromic acid were added. There was no apparent reaction at the interface between the aqueous and non-aqueous layers (the aldazinium compounds had precipitated at the interface) and the solutions were allowed to stand for 48 hours. No product was obtained other than the azine which had crystallised out. 0.2 g. of the azine was dissolved in nitrobenzene and treated with hydroiodic acid. No product was obtained.

0.23 g. of the azine was dissolved in hot xylol and treated with a stoichiometric quantity of 98% sulphuric acid in ether. A small yield of white product was obtained which was allowed to stand in the solution at -10°C for 3 weeks. The crystals (mainly yellow flecked with white) were separated, washed with ether and analysed. Found N_2H_4 6.5; SO_4 23.6%. This gives a hydrazine: sulphate ratio of 1:1.2.

The azine monosulphate requires N_2H_4 7.6; SO_4 22.8%, and the azine disulphate requires N_2H_4 6.1; SO_4 36.8%. This is possibly a mixture of the two. Similar results were obtained with o-hydroxy acetophenone (see below).

o-HYDROXY ACETOPHENONE AZINE.

0.1 g. portions of the azine dissolved in ether were treated in turn with dry hydrochloric acid gas; 48% hydrobromic acid and 50% hydroiodic acid. No products were obtained with any of these reagents.

Approx. 0.1 g. of the azine dissolved in ether was treated with the stoichiometric amount of 98% sulphuric acid dissolved in ether. There

was no immediate result but after standing at -10°C for a few days yellow crystals separated. These were washed with ether, dried and analysed. Found N_2H_4 7.3; SO_4 25.4%. This gives a hydrazine to sulphate ratio of 1:1.16 which agrees very closely with that obtained from the compound made from m-nitro acetophenone azine.

p-METHOXY ACETOPHENONE.

0.3 g. of the azine was dissolved in 50 c.c. of benzene which was warmed slowly. The azine dissolved at 55°C and the solution was then brought up to 60-65°C and held in this temperature range. Dry hydrochloric acid gas was passed through the solution for 30-35 minutes, and a yellow product obtained. This was separated and washed twice with benzene and twice with ether. Yield 0.21 g., m. pt. 186-190°C. Tests for the presence of chloride gave positive results. N_2H_4 was found to be 10.63%. The azine hydrochloride requires 9.57% N_2H_4 whereas the azine requires 10.74% N_2H_4 and melts at 200-201°C. The product therefore appeared to be impure azine.

0.2 g. of the azine was dissolved in benzene and the stoichiometric amount of 98% sulphuric acid in ether added. A yellow powder flaked with white resulted immediately. This was separated, washed with ether and analysed. N_2H_4 found to be 7.6%, the azine sulphate requires N_2H_4 8.1%. On standing in a desiccator overnight the crystals changed colour from yellow to salmon pink. On treating with barium chloride a mixture of crystals separated.

BENZOPHENONE AZINE.

The total crop of crystals obtained in the first azine preparation (from ethanol) 0.13 g. dissolved in ether, was treated with the calculated weight of 98% sulphuric acid in ether. On adding the sulphuric acid ether solution the mixture became cloudy, the cloudiness, however, disappeared on adding the remainder of the acid. The mixture was left standing at -10°C but no salt was obtained.

Dry hydrochloric acid was passed into the mother liquor from which the crystalline azine had been obtained. The solution became appreciably hot, the temperature rising approximately 80° (from ± -5° to ± 75°C). A yellow oil separated and the mixture was kept at -10°C. The solution was shaken regularly over the course of a month but no crystallisation could be induced. It was therefore decided to separate the oil from the alcohol solution and attempt a recrystallisation from another solvent. On opening the flask containing the solution, there was a sudden release of pressure and hydrochloric acid fumes were given off. Immediate crystallisation took place, the whole solution setting solid.

The solid was filtered off and the solvent squeezed out. Ether dissolved the crystals, so they were washed with absolute alcohol and dried over calcium chloride in the presence of stick sodium hydroxide. On analysis no hydrazine was found to be present. The chloride content was 1.7%. Testing with di-nitro-phenyl hydrazine (d.n.p.) gave positive results. The substance melted at 48-48°C, i.e. was benzophenone contaminated with hydrochloric acid, the azine having hydrolysed in the alcohol in the presence of hydrochloric acid.

The liquid obtained from the second azine preparation (ex chloroform) was dissolved in 10 c.c. of ether and dry hydrochloric acid gas passed through the solution. A white solid (yield 2 g.) resulted. This was washed twice with ether, dried and analysed. M. pt. 166-168°C. Found N_2H_4 8.1; Cl 9.0%. Diphenylketazine hydrochloride requires N_2H_4 8.1; Cl 9.2%.

ACETONE KETAZINE.

0.4 g. was dissolved in ether and treated with the stoichiometric amount of 98% sulphuric acid. The solution became cloudy and an oil separated. The oil became viscous on standing at 10°C and was centrifuged off and allowed to dry. Analysis showed it to be impure mono hydrazine sulphate.

0.5 g. of the azine dissolved in ether was treated with 48% hydrobromic acid. The mixture was cooled in ice and a few crystals formed which disappeared on standing. The preparation was repeated the crystals this time were separated immediately, washed once with ether and analysed. They proved to be hydrazine dihydrobromide. Treating the azine dissolved in ether with dry hydrochloric acid gas yielded hydrazine dihydrochloride.

ETHYL METHYL KETAZINE.

0.52 g. of the azine was dissolved in ether and treated with the calculated weight of 98% sulphuric acid. The mixture became cloudy and an oil settled out. After standing at -10°C for a week, the ether was allowed to evaporate off and a viscous yellow product remained. This was allowed to stand over concentrated sulphuric acid until it had

hardened and was then analysed. The compound proved to be impure hydrazine disulphate.

The azine dissolved in nitrobenzene and treated with 48% hydrobromic acid gave hydrazine dihydrobromide, and treating an ethereal solution of the azine with hydrochloric acid gas yielded hydrazine dihydrochloride.

di-n-PROPYL KETAZINE.

The ketone was dissolved in anhydrous ether and treated with a solution of 95% hydrazine in dry ether. The mixture became cloudy but cleared on standing. Hydrochloric acid gas passed through a few milliliters of the clear solution gave an immediate white precipitate which on analysis appeared to be impure hydrazine dihydrochloride. A further few cubic centimeters of the solution was taken and treated with dry hydrochloric acid gas. White product was again obtained which on analysis proved to be almost pure hydrazine dihydrochloride.

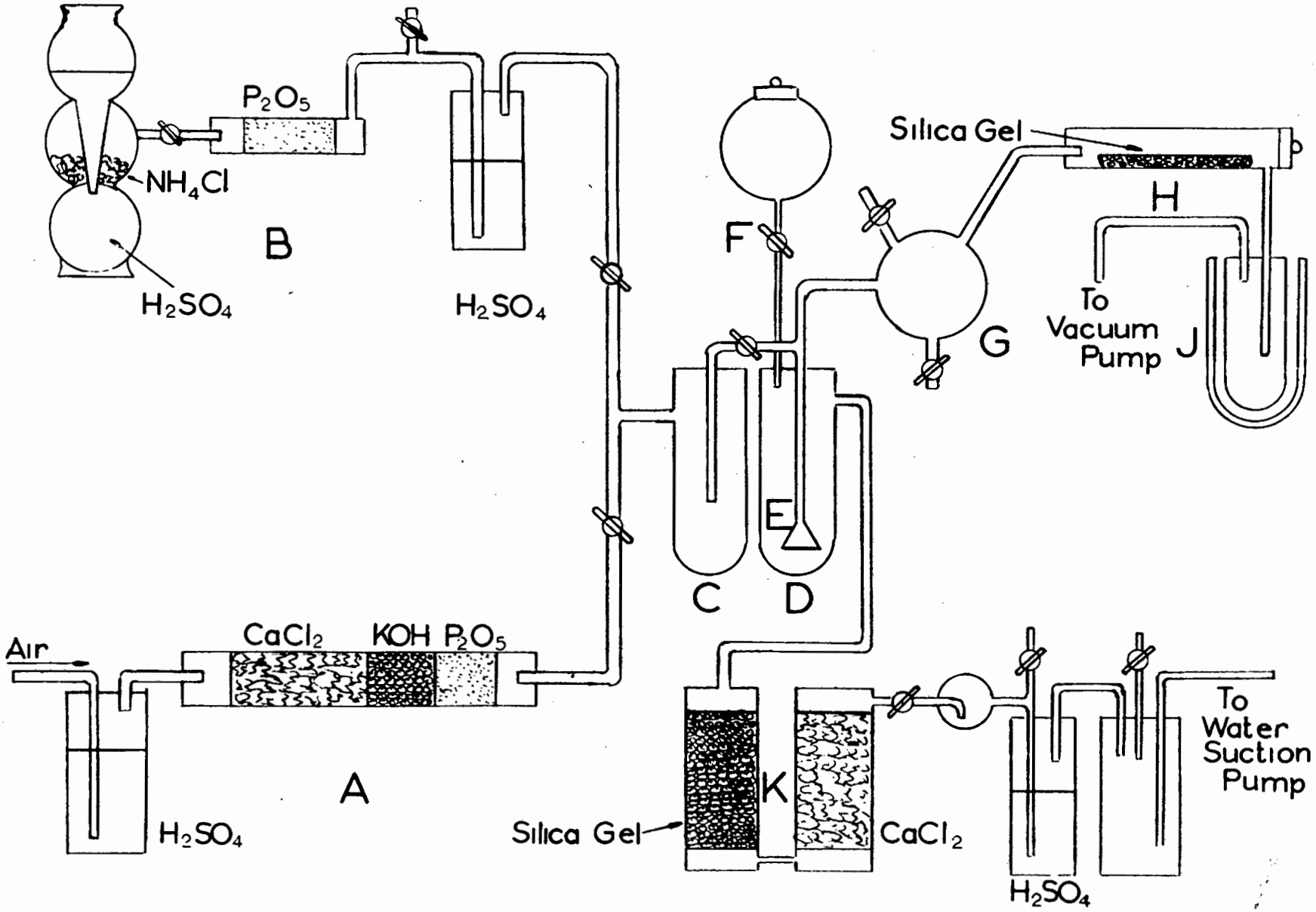


Fig 1 Vacuum Train

CONSTRUCTION OF VACUUM TRAIN.

As the failure to obtain compounds might have been due to hydrolysis it was decided to repeat some of these preparations under strictly anhydrous conditions.

A train was constructed (see Fig. 1) in which all the operations i.e. preparation, filtration, washing, recrystallisation, etc. could be carried out with moisture rigorously excluded.

The apparatus consisted of a train (A) to dry the air used for flushing the apparatus. The rate of flow was controlled by a screw clip and the incoming air passed successively through concentrated sulphuric acid, calcium chloride, potassium hydroxide and phosphorus pentoxide. Train (B) produced the dry hydrochloric acid gas. The gas was produced from ammonium chloride and sulphuric acid in a Kipp's apparatus and was dried by passing it through phosphorus pentoxide and concentrated sulphuric acid. Both of these trains led into a vessel (C) fitted to the train by means of a ground glass joint. (This vessel contained solvent for washing the filter plate in the reaction vessel after the reaction was complete), and thence to the reaction vessel (D) via a filter plate (E). A separating funnel (F) used for introducing either starting materials or wash liquids led into this vessel and from it an outlet tube led to another drying train (K), then through a splash bulb to a sulphuric acid drying tower (to remove water vapour from the suction pump), and finally through a water trap to a water suction pump. Air inlets were provided on either side of the sulphuric acid containers to minimise sucking back when the suction

pump was turned off. Suction for filtering was obtained from a rotary vacuum pump protected by a liquid oxygen trap (J). This section of the apparatus was connected to the filter plate via a tube containing self-indicating silica gel (which could be replenished easily through a ground glass end) and a separating funnel (G) from which the filtrate could be removed. Filtrate was only removed if absolutely necessary, as, due to the vacuum in the apparatus, liquid would only run out with difficulty.

PREPARATIONS UNDER STRICTLY ANHYDROUS CONDITIONS:

ACETONE KETAZINE.

The azine dissolved in anhydrous ether (made by distilling ether mixed with sulphuric acid and drying the distillate over sodium) was introduced into the reaction vessel (G). Dry air was sucked through the apparatus for 15 minutes and then dry hydrochloric acid gas was passed through the solution. For the first 10-15 minutes nothing was observed and then suddenly dense white fumes appeared. This was followed by the separation of a yellow oil. The gas was passed through for a further 15 minutes.

The ether was sucked off and removed at (G). Dry cyclohexane was introduced via the dropping funnel (F) (to recrystallise the oil if possible), and the reaction vessel was heated to 60-65°C (by surrounding it with water held in this temperature range). On cooling, yellow crystals appeared. The cyclohexane was filtered off, the crystals were removed, washed with ether and dried. Analysis gave no free

hydrazine, negative results were obtained on testing for ketone with dinitro phenyl hydrazine. Chloride was found to be 22.9%. Both acetone ketazine hydrochloride and pyrazoline hydrochloride require 23.8% chloride. The crystals were recrystallised from absolute alcohol and a melting point taken. Found 175-176°C. Pyrazoline hydrochloride melts at 175-177°C. The ketazine had ring closed under the influence of heat and the ring closed product had formed the simple chloride salt.

As heating had caused ring closure it was decided to repeat the preparation keeping the reaction vessel cold.

The azine dissolved in dry ether was placed in the reaction vessel which was surrounded by dry ice. Air was sucked through the apparatus for approximately 10 minutes and then the hydrochloric acid gas was introduced, air being pulled through the apparatus at the same time. After a minute or two dense white fumes began to form in the reaction vessel which became less dense with time and ultimately disappeared after about 8 minutes. Hydrochloric acid gas was passed for 2-3 minutes longer and then air alone was allowed to flow for a further 2 minutes. The dry ice was removed and the air flow continued to aid the evaporation of the ether. As the reaction vessel warmed to room temperature a yellow oil began to appear which slowly settled to the bottom. After about 10 minutes the air supply was cut off and the apparatus was left under suction for 30 minutes. During this period dry ice was again placed around the reaction vessel. By this stage almost all the ether had been removed and the liquid inside the reaction vessel was a cloudy yellow. The liquid was removed from

the reaction vessel as quickly as possible and the bulk of it, unfiltered and unwashed, placed in the deep freeze. The remainder was found to be insoluble in cyclohexane or xylol. It appeared to dissolve in water, but on standing the solution separated into two layers; an oily yellow layer and an aqueous layer containing a few cream-white crystals. The crystals proved to be hydrazine dihydrochloride. The oily layer dissolved in 99% ethanol and gave a clear yellow solution, this was kept at -10°C for 15 hours with no apparent result. On standing at room temperature, however, a crop of cream coloured crystals separated which proved to be hydrazine dihydrochloride.

The bulk of the solution after one week at -10°C had set solid, on being brought up to room temperature a viscous mass (1.02 g.) resulted. This was dissolved in 100 c.c. of water (in this considerable excess no oily layer separated) and was analysed. A positive d.n.p. reaction was rapidly obtained. N_2H_4 was found to be 13.5% and Cl 31.3%. The hydrazine: chlorine ratio being 1:2. This was probably a mixture of hydrazine dihydrochloride and acetone, as the presence of ketazine would have given a high hydrazine value and not a low one.

ETHYL METHYL KETAZINE.

The azine dissolved in dry ether was introduced into the reaction vessel and cooled to 0°C. Dry air was sucked through the apparatus for 40 minutes and then the hydrochloric acid gas introduced. After about two minutes white fumes appeared. (cf. Previous attempt, it is possible that this is the time taken for the hydrochloric acid gas

to reach the reaction vessel). After about 5 minutes a dark yellow oil began to separate. After a further 5 minutes the fumes had ceased, and the oil had changed colour from yellow to red-brown. The HCl gas was stopped after 15 minutes and the air continued for a further 5 minutes. The viscous oil was removed from the reaction vessel and a few crystals found to be present were filtered off as rapidly as possible. Both the liquid (in a stoppered weighing bottle) and the crystals were kept over sulphuric acid.

The liquid was insoluble in ether whereas the original azine (pale yellow in colour) had been completely miscible. The oil dissolved in water to give a golden yellow solution and treatment with d.n.p. reagent showed the presence of ketone. Hydrazine titrations on different samples showed in turn 22.9, 13.1 and 12.7%. Chloride on the last sample was 26.4%. The azine hydrochloride requires N_2H_4 18.1, Cl 20.1%. At this stage the oil started showing a marked difference in appearance and was obviously decomposing. The crystals would not dissolve in water, gave positive results with d.n.p. reagent and N_2H_4 was found to be 28.5%. They were probably (on analysis figure) hydrazine dihydrochloride contaminated with ketone. This salt dissolves very easily in water, however, and it seemedunlikely that traces of the ketone should affect its solubility. The liquid was refluxed with xylol (with which it was immiscible) and dense white fumes were given off. A tar formed which was discarded. It was decided to repeat this experiment at a lower temperature and to avoid decomposition of any product as much as possible by dissolving

the entire yield in water and then to analyse aliquots.

The ketazine, without solvent, was placed into vessel (C) which was to be used as the reaction vessel. The reaction vessel was surrounded with liquid oxygen so that the ketazine was frozen solid, the oxygen level being not appreciably higher than the top of the ketazine in the reaction vessel. Dry air was sucked through the apparatus for 10-15 minutes and then dry HCl gas introduced. After about 10 minutes the "Dewar" flask containing the liquid oxygen was removed. The hydrochloric acid had formed a solid layer above the azine. This liquified very rapidly and the HCl supply was closed off. As the HCl vaporised and the ketazine liquified a vigorous reaction took place. The azine layer changed in colour from straw yellow to a deep golden in the course of 10-12 minutes. At this stage the liquid became opaque and bubbles were still coming off, but very slowly. After a further 5 minutes the bubbling had all but ceased, and after another 20 minutes the product was very viscous (or appeared so), containing either another liquid or a finely divided solid in suspension. Its colour had deepered to a light brown. The vessel was removed from the train and the product transferred as rapidly as possible to a weighing bottle (previously weighed), weighed and dissolved in distilled water. The solution was then made up to 100 c.c. On being exposed to the air pungent fumes were given off instantly and on being dissolved in water a white solid was formed (N_2H_5Cl ?) which dissolved in excess water. The total time from opening the train to making the standard solution was 3 minutes.

sudden surge occurred before the reaction was complete. The turbidity might be explained by the breakdown of unchanged azine into ketone and hydrazine giving a second liquid phase. This would explain the positive d.n.p. and the presence of hydrazine hydrochloride. It would also account for the low figure obtained for the hydrazine titre. If a ring closed product had been formed there was the possibility that a chloroplatinate might be obtained, it had been shown that pyrazoline formed a chloroplatinate (see below).

20 c.c. (≡ 0.3 g.) of the solution of the supposed ring closed product was taken and treated with 18 c.c. of M/40 potassium iodate solution. This (on the analysis figures) would remove all the free hydrazine. It was then added to a solution of chloroplatinic acid (equivalent to 0.2 g. of platinum) in excess dilute hydrochloric acid. Nothing appeared to happen and the solution was evaporated to dryness on a water bath.

A brown viscous product containing a large quantity of colloidal platinum resulted. On close examination red crystals were seen present in the brown oil. Repeated flotations (12 in all) with water isolated the crystals which were oven dried at 95°C for 15 minutes. Yield was 17 milligrams, M. pt. 179-181°C.

Testing with dinitrophenyl hydrazine gave no crystalline product therefore ketone was absent. Treating with silver nitrate and nitric acid yielded a yellow precipitate which indicated the presence of the chloroplatinate ion. Flame test indicated the presence of potassium, but no confirmation was obtained on treating a few drops of a solution

On analysis N_2H_4 was found to be 12.5% (cf previous case 12.7%), and the chloride 39% (higher than previous case). The ratio of hydrazine: chlorine being 1:2.8. An immediate reaction with d.n.p. reagent was obtained. The product smelt similar to ethyl methyl ketone, there was no trace of the characteristic ketazine odour.

What might possibly have happened was that ring closure had taken place to some extent,and that some of the unchanged azine had been decomposed forming ketone together with hydrazine hydrochloride.

The previous experiment was repeated. The liquid oxygen surrounding the reaction vessel was lowered very slowly and the ketazine melted slowly. The resultant liquid darkened slowly. As the top of the "Dewar"flask containing the oxygen came below the level of the ketazine, there was violent reaction with a pressure surge which blew the end out of the drying chamber (H) in the vacuum pump train. The reaction vessel was removed immediately and clouds of acrid fumes were given off (HCl),the liquid in the vessel bubbling furiously. The bubbling ceased after a few minutes, and the clear red-brown liquid which resulted was transferred to a weighing bottle and weighed. During the weighing it began to become turbid. The liquid was transferred to a standard measuring flask and made up to 100 c.c. with distilled water. On the initial addition of water, hydrazine hydrochloride was precipitated, but not in any appreciable amount. Analysis gave N_2H_4 3.9, Cl 14.6% which gives a hydrazine to chlorine ratio of 1:3.4. The liquid left in the reaction vessel when tested with d.n.p. reagent showed the presence of ketone. Probably the ketazine was ring closing and the

of the compound with sodium cobaltinitrite solution.

A combustion analysis on 12 milligrams gave C, 0; H, 2-3; and Pt of the order of 50%. No greater accuracy was possible on the quantity handled.

Hydrazine chloroplatinate prepared by Thiele (1892)[35] requires H 2.2; Pt 43.7%. No m. pt. given. A melting point determination was done on a sample of pure hydrazine chloroplatinate (containing half a mol. of water per mol. of chloroplatinate) prepared by Mr. M.C.B. Hotz for conductance measurements[36] on hydrazine salts. The salt decomposed at 206°C with reduction of the chloroplatinate. Potassium chloroplatinate might have been formed (the potassium from the iodate solution reacting with the chloroplatinic acid). This salt was yellow in colour, had no hydrogen, platinum of the order of 40% and decomposed at 250°C. Potassium chloroplatinate is red-brown in colour, also has no hydrogen, has platinum of the order of 47% and decomposes on heating, no temperature is given.

To see whether a product of similar melting point could be obtained by treating the ketazine with chloroplatinic acid, a few c.c. of the chloroplatinic acid solution was added to a solution of the ketazine. No apparent reaction was noticed apart from the production of colloidal platinum. The platinum was centrifuged down and the clear solution decanted off and evaporated to dryness on the water bath. A red-brown amorphous product was obtained which decomposed in the range 181-186°C. On attempting to recrystallise this mixture (solvents alcohol, water,

ethyl methyl ketone) decomposition with the formation of colloidal platinum took place. Subsequent attempts to prepare complex platinum salts with ethyl methyl ketazine led to similar results and to the formation of what appeared to be co-ordination compounds (see below).

DI-ETHYL KETAZINE AND DI-BUTYL KETAZINE.

Similar preparations were tried with the above, the reaction vessel being kept at 0°C. No product other than hydrazine hydrochloride was obtained.

Mrs. Sohn (loc. sit) had, concurrently with this work, attempted to make simple hydrochlorides of n-propaldazine and n-butaldazine, using the same apparatus. She had also met with no success and it seemed reasonably certain that if these simple salts with aliphatic ketazines did exist, they were most unstable under normal conditions and decomposed in the presence of the slightest trace of moisture.

AZINE CONSISTING OF 1 MOL. OF ACETONE AND 1 MOL. OF ACETOPHENONE WITH 1 MOL. OF HYDRAZINE.

The iodide and bromide of a base made by condensing 1 mol. of acetone, 1 mol. of benzaldehyde and 1 mol. of hydrazine had been prepared by Mrs. Sohn, and it seemed possible that similar compounds might be made from a mixed base made from hydrazine condensed with acetone and acetophenone. The hydrazone of acetone was prepared by the method of Curtius and Pflug (loc. sit.) on being treated with acetophenone (1 mol. for each mol. of acetone) no apparent reaction was noted. On being left at -10°C for 8 weeks yellow crystals were obtained. These proved to be impure acetophenone azine crystals.

It was therefore decided to try to get the salts by mixing the two ketones, hydrazine, and the acid. This method had proved successful in the case of acetone-benzalazine, the salts of the mixed azine being the least soluble product. Acetophenone azine was dissolved in excess acetone. To half the solution was added a solution of hydroiodic acid in acetone and to the other half a solution of hydrobromic acid in acetone.

The solutions were kept at 0°C but no product was obtained. The solutions were then heated on the water bath and allowed to cool. With the hydroiodic acid no product was obtained, with the hydrobromic acid a black oil was formed which could not be analysed. The previous "mixed base" had been made by treating benzalazine with acetone. The work was repeated by taking acetone ketazine and treating this with benzaldehyde. Both the iodide and the bromide were prepared without any difficulty.

CYCLOHEXANONE AZINE.

The yellow oil thought to be cyclohexanone azine (it had decomposed when attempts were made to analyse it or to find its boiling point) was treated with dry hydrochloric acid in an attempt to make the hydrochloride. No product could be isolated. Treating with hydroiodic acid and with hydrobromic acid also yielded no product,

(iii) Preparation of the fluorogallates and fluoroindates of hydrazine.

Before preparing the complex fluorogallates and indates described below, attempts were made to prepare the other halegeno-gallates and indates.

With the exception of gallium triiodide the trihalides were not isolated. They are all very deliquescent and the syrups obtained after the final evaporation (see Starting Materials, p. 38) were used as starting materials. The amount of gallium or indium originally taken was known and the stoichiometric quantities of other reagents were calculated using these weights.

With the bromides and iodides the relatively less soluble hydrazine salt always precipitated first. With the chlorides this also occurred with the exception of one preparation when a ratio of hydrazine to chloride of 1:6 was obtained. Gallium could not be determined owing to the volatility of the gallium chloride.

Meanwhile X-Ray diffraction studies of the hexachloroaluminate had been made by the Department of Physics, University of Cape Town. A personal communication has indicated that the salt thought to be the hexachloroaluminate is not the compound reported, the chlorides not being co-ordinated about the central metal ion.

The complex chloro-, bromo- and iodo- gallates and indates of hydrazine therefore do not appear to exist. The compounds obtained being mixed, hydrated salts which have precipitated together from solution.

(a) The Fluorogallates of Hydrazine.

Gallium hydroxide (equivalent to 0.44 gm. Ga) prepared by precipitation from gallium residues was treated with 2.5 gm. of 34% w/w hydrofluoric acid. A white powder resulted which dissolved in 30 c.c. of water on being heated on the water bath for 5 hours.

The volume of the solution was reduced to 10 c.c. and 2.2 gm. of 10% hydrazine hydrate, which had been diluted to 25 c.c. and made acid with HF, was added. The mixed solutions were allowed to stand with no apparent result. Reducing the volume to half also produced no results, but after a further reduction in volume, product was obtained on seeding with solid product obtained by evaporating a few drops of the solution to dryness. A second crop was obtained on evaporating the mother liquor to dryness.

Analysis of these products gave hydrazine 9.9, gallium 27.85 and fluoride 37.6%. These did not fit any expected formula and gave a ratio of N_2H_4:Ga:F::0.8:1:9.

Gallium hydroxide (equal to 0.43 gm. of Ga) was treated with 1.3 gm. of 34% HF. The hydroxide did not dissolve easily as in the previous attempt, and solution could only be effected on adding an extra 2.3 gm. of HF. A solution of 6 gm. of 10% hydrazine hydrate, made acid with HF, was added to the gallium-fluoride solution and on cooling a white solid separated. This was dried over sulphuric acid (with a 2% loss in weight) and then analysed. Yield 3.2 gm. Analysis gave hydrazine 16.1, gallium 26.6 and fluoride 57.2%. These figures did not fit any expected formulation and gave a ratio of N_2H_4:Ga:F::1.3:1:8.8.

The gallium:fluoride ratio was similar in the two preparations, hydrazine was, however, lower in the first. All the product of the first preparation that remained after analysis (approximately 1 gm.) was dissolved in water, made acid with HF and treated with 2 gm. of 10% hydrazine hydrate. After being warmed on the water bath and then being allowed to cool slowly, the solution yielded a white substance which contained 16.4% hydrazine, a result very similar to that obtained for the second preparation.

The substance obtained in the second preparation (1 gm.) was dissolved in 5 c.c. of warm water and the solution was allowed to cool slowly. No product was obtained and the volume was reduced by evaporation. When the volume had decreased to approximately 1 c.c. crystals were obtained. The mother liquor was decanted and the product dried under vacuum over concentrated sulphuric acid. On examination, using a hand lens, two distinct types of product were seen. A few large translucent crystals which were removed by hand and on analysis gave N_2H_4 9.8% (cf. first preparation) and a white powder which gave N_2H_4 16.8, Ga 32.2, F 60.8%. $N_2H_6GaF_4.3HF$ requires N_2H_4 13.4, Ga 29.2, F 63.6%.

Gallium trifluoride trihydrate was prepared and analysed. 1 gm. was taken and dissolved in 30 c.c. of 20% HF. 5.4 gm. of 10% (w/w) hydrazine hydrate (equivalent to three molecules of hydrazine to one molecule of gallium) was made acid with HF, and this solution was added to the gallium trifluoride solution and heated on the water bath. When the volume had been reduced to 20 c.c. a white powder separated

and further concentration to approximately 5 c.c. yielded a second crop of product. A third crop was obtained on taking the solution to dryness.

The second crop, which was likely to be the purest, was analysed. Obtained N_2H_4 13.0, Ga 15.1, F 69.5%. $(N_2H_5)_2$ GaF_5.11 HF requires N_2H_4 14.2, Ga 15.46, F 67.45%.

All three crops of product were digested in 5 c.c. of water for half an hour. On cooling a crop of solid product was obtained, the bulk of the substance, however, being recovered only on evaporation to dryness. Analysis gave N_2H_4 9.2, Ga 19.8, F 71.5%. $N_2H_5GaF_4$.10HF requires N_2H_4 8.44, Ga 18.42, F 70.3%.

To reduce the chance of adsorbed HF being present, gallium trifluoride trihydrate and hydrazine dihydrofluoride were used as starting materials. 0.6 gm. of gallium trifluoride, trihydrate was dissolved in water and 0.24 gm. of hydrazine dihydrofluoride was added. The solution was concentrated almost to dryness and allowed to cool. Prolonged standing did not yield any product. Further concentration gave a very viscous syrup which yielded solid product on being evaporated to dryness. Analysis gave N_2H_4 14, Ga 29.4, F 45.3%. $N_2H_5GaF_4$.2HF requires N_2H_4 14.64, Ga 31.85, F 52.2%. N_2H_5 GaF_4.HF requires N_2H_4 16.13, Ga 35.2, F 47.8%.

This preparation having given promising results, the next was carried out using hydrazine monohydrofluoride instead of hydrazine dihydrofluoride. 1 gm. of gallium trifluoride trihydrate was dissolved in 30 c.c. of warm water, and to this solution was added

a solution of 0.6 gm. of hydrazine monohydrofluoride in 10 c.c. of water. The mixed solutions were allowed to cool, but no solid separated on standing for twenty-four hours. The solution was evaporated down very slowly, but no product was obtained until it had been taken completely to dryness. The substance obtained was very soluble in water and attempts to recrystallise it from acetone led to the formation of a viscous oil that could not be handled.

The preparation was repeated using hydrazine dihydrofluoride. 3 gm. of gallium trifluoride trihydrate and 1 gm. of hydrazine dihydrofluoride were dissolved separately in water. The two solutions were mixed and heated on the water bath. Solid product (yield 3.4 gm.) was obtained before the solution had been evaporated completely. Analysis gave N_2H_4 11.5, Ga 28.6, F 34.75%. The total figure did not add up to 100% even after allowance for hydrogen, etc., had been made, and it seemed likely that water of crystallisation was present. The difference was equivalent to four molecules of water of crystallisation. $N_2H_5GaF_4.HF.4H_2O$ requires N_2H_4 11.7, Ga 25.42, F 34.6%. The substance was too soluble to recrystallise from water, and as the use of acetone had led to a viscous oil being formed in the previous preparation, ethyl alcohol was used for the recrystallisation. Here again an oil resulted which dried to give a vitreous glass-like solid. This was dissolved in water and the resulting solution evaporated to dryness. A white substance was obtained which was dried under vacuum, over sulphuric acid, for 72 hours and then analysed.
Analysis gave N_2H_4 21.4, Ga 32.5, F 30.7%. Assuming water present these give a ratio $N_2H_4:Ga:F:H_2O::1.47:1:3.47:1.9$, result which were

unexpected and inexplicable.

1.5 gm. of gallium trifluoride trihydrate and 0.5 gm. of hydrazine dihydrofluoride were dissolved separately in water. The solutions were mixed and heated on the water bath. On evaporating the solution to dryness a white substance was obtained which was dried under vacuum, over sulphuric acid, for 72 hours and was then analysed. Found N_2H_4 29.98, Ga 30.9, F 29%. Here again the totals did not add up to 100% and water was assumed present. The analysis gave the ratio N_2H_4 : Ga : F : H_2O :: 2.1 : 1 : 3.5 : 1.2. These figures are unexpected as although the Ga:F ratio is what is expected (1:4), the hydrazine is very high; one would expect only one molecule of hydrazine associated with a GaF_4^- ion.

Further preparations were again carried out in acid solutions. 1.5 gm. of gallium trifluoride, trihydrate was dissolved in 100 c.c. of 10% HF solution, and to this solution was added 0.6 gm. of hydrazine dihydrofluoride dissolved in 25 c.c. of water. The mixture was heated on the water bath and a crop of crystals was obtained when the volume of the solution had been reduced to approximately 20 c.c. After standing for 48 hours, almost all the water had evaporated and a large crop of product was obtained. The yield was 1.7 g., which was more than the weight of the starting materials, indicating that water or HF had come down with the product. Analysis gave N_2H_4 15.2, Ga 31.6, F 51.8%. $N_2H_5GaF_4.2HF$ requires N_2H_4 14.64, Ga 31.85, F 52.2%.

The next preparation followed the technique which had been used successfully for the preparation of the ammonium penta- and hexa-

fluoroaluminates, namely boiling aluminium hydroxide in an aqueous solution of ammonium fluoride.

0.1 gm. of gallium as the oxide was dissolved in aqua regia and the hydroxide precipitated with ammonia solution. The hydroxide was separated by centrifuging, washed with distilled water and dissolved in a solution of 0.4 gm. of hydrazine dihydrofluoride in water, i.e. an excess of fluoride.

A vitreous deposit was obtained when the solution was evaporated to dryness. This was dissolved in a few c.c. of water and allowed to stand; after 48 hours a gelatinous substance was seen to be present, some of the original product having dissolved. The gelatinous precipitate was separated, and on being dried yielded 0.3 gm. of a grey-like substance. The mother liquor was evaporated to dryness on the water bath, and a deliquescent white powder resulted which was dried over sulphuric acid.

The gelatinous substance on analysis gave N_2H_4 5.1; Ga 16.4 and F 60.8%. Assuming that water is present we get a ratio N_2H_4 : Ga : F : H_2O :: 2 : 3 : 42 : 12. The product could possibly be a mixture of one molecule of gallium trifluoride trihydrate and two molecules of $N_2H_6GaF_4.14.5HF,4\ H_2O$.

The product obtained by evaporating the mother liquor to dryness gave N_2H_4 28.9, Ga 35.2 and F 35.1%. This gives a ratio of N_2H_4 : Ga : F :: 1.8 : 1 : 3.8. While the Ga:F ratio is what one would expect, the hydrazine is twice that expected. These results

are very similar to those obtained earlier when gallium trifluoride in solution was treated with hydrazine dihydrofluoride solution.

1.5 gm. of gallium trifluoride trihydrate was dissolved in 100 c.c. of 10% HF solution and this solution was treated with 0.6 gm. of hydrazine dihydrofluoride dissolved in 25 c.c. of water. The mixed solution was heated on the water bath and when the bulk had reduced to about 10 c.c. solid product precipitated. The solution was allowed to cool and the mother liquor was decanted. The precipitate was washed with 1 - 2 c.c. lots of water and the washings were added to the mother liquor. The mother liquor was evaporated to dryness and another crop of product was obtained. The products were very moist and were dried under vacuum. A large volume of HF was given off which completely etched the desiccator. The first crop on analysis gave N_2H_4 12.45, Ga 13.85, F 72.5%. $(N_2H_5)_2\ GaF_5$, 14.5HF requires N_2H_4 12.26, Ga 13.36, F 71.0%. The product obtained by evaporating the mother liquor to dryness gave on analysis N_2H_4 11.64, Ga 16.1, F 59.5%. There is some 12% unaccounted for; if this is assumed to be fluoride the compound obtained could be $(N_2H_5)_2\ GaF_5$, 11HF, on the other hand if it is assumed to be water, the compound could be $(N_2H_5)_2\ GaF_5$, 9HF, $2H_2O$.

A final large scale preparation was carried out as follows: 12.6 gm. of the oxide was treated with an excess of 50% (w/w) HF and evaporated to dryness. This was repeated five times. The powder obtained was treated with HF (large excess of the weight theoretically required) and then with 4 c.c. of 95% hydrazine solution. The

mixture was taken to dryness and then extracted four time with 250 c.c. lots of water. After the fourth extraction a negligible quantity of solid remained.

The solutions resulting from the extractions were mixed and concentrated on the water bath; when the volume had reduced to 100 c.c. a crop of crystals separated. Yield 5 gm. Microcrystalline needles often joined to give a fan-like group. Further concentration to 25 c.c. gave a second crop of 13.5 gm. which were also micro-crystalline. Evaporation to dryness yielded 2.5 gm. of an amorphous powder.

Crop 1 analysed to give N_2H_4 17.3, Ga 30.7, F 43.5%. Crop 2 analysed to give N_2H_4 13.1, Ga 28.95%, F 40.75%. Crop 3 gave N_2H_4 12.1, Ga 32.9, F 40.3%. N_2H_5 GaF_4.HF.$2H_2O$ requires N_2H_4 13.5, Ga 29.4 and F 40.1%. Crop 2 was was to be expected was the purest. However, all the crystals appeared to be the pentafluorogallate sought.

(b) The fluoroindates of hydrazine.

The first preparation attempted was by an analogous method to that used to prepare the ammonium fluoroindate, namely treating the chloride with ammonia solution and then treating the solution with hydrofluoric acid.

1 gm. of indium chloride was dissolved in 10 c.c. of water, an excess of hydrazine hydrate was added, and the solution was made acid with hydrofluoric acid. On concentrating the solution a number of crops of crystals were obtained, these all proved to be hydrazine dihydrofluoride.

The next preparation attempted was with the trifluoride. 1 gm. of indium trifluoride trihydrate was dissolved in water and the solution made acid with hydrofluoric acid. This solution was treated with the theoretical amount of 60% hydrazine hydrate (heat was generated on mixing) and a white precipitate formed which disappeared on stirring. On standing for 72 hours a crop of crystals was obtained, and a second crop was obtained when the mother liquor was evaporated to dryness. Both crops of crystals proved to be hydrazine dihydrofluoride.

0.5 gm. of indium trifluoride trihydrate was dissolved in 5 c.c. of water and 2 c.c. of 48% (w/w) HF and 0.2 gm. of hydrazine dihydrofluoride was added. This dissolved immediately and the solution was allowed to cool. On standing a white amorphous powder separated which on analysis gave N_2H_4 7.9, In 18.2, F 72.8%. $(N_2H_5)_2$ InF.17.5HF requires N_2H_4 10.88, In 19.48, F 66.3%, i.e. the product appears to the above salt contaminated with hydrazine dihydrofluoride.

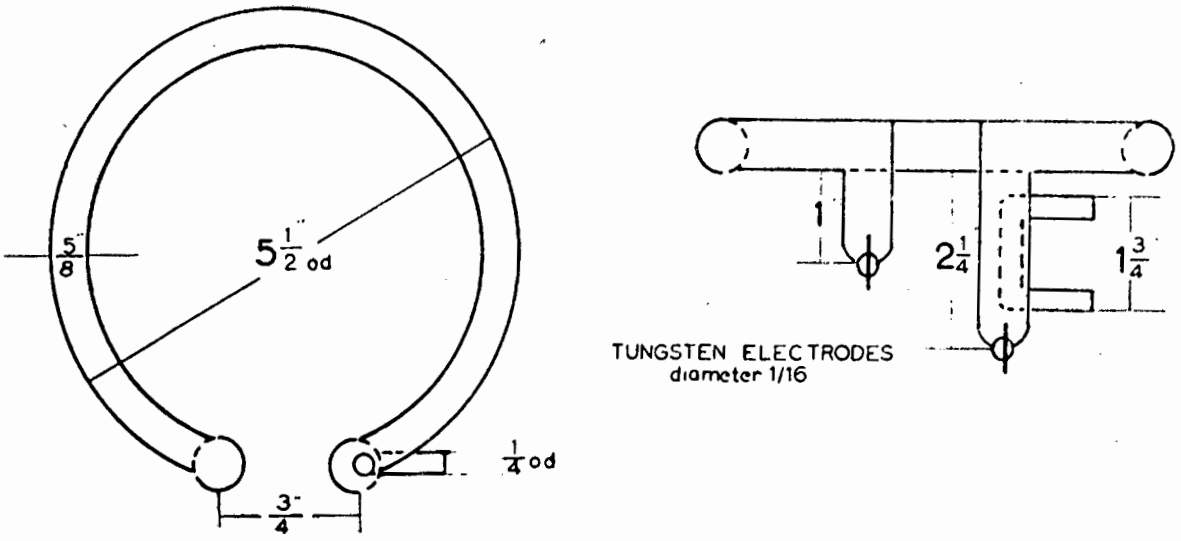
A further 1.2 gm. of indium trifluoride trihydrate was dissolved in water and was treated with 0.38 gm. of hydrazine dihydrofluoride. On concentrating the solution almost to dryness a yield (0.86 gm.) of a white substance was obtained, which on analysis gave N_2H_4 27.7, In 28.2, F 47.7%. These give a ratio N_2H_4 : In : F :: 7 : 2 : 42, which could be explained by the product being a mixture of five molecules of hydrazine dihydrofluoride and two molecules of N_2H_5 InF_4, 12HF.

3 gm. of indium trifluoride trihydrate were taken and attempts were made, unsuccessfully, to dissolve this in 1 litre of water. This was rather surprising as Ensslin and Dreyer[57] had quoted the solubility

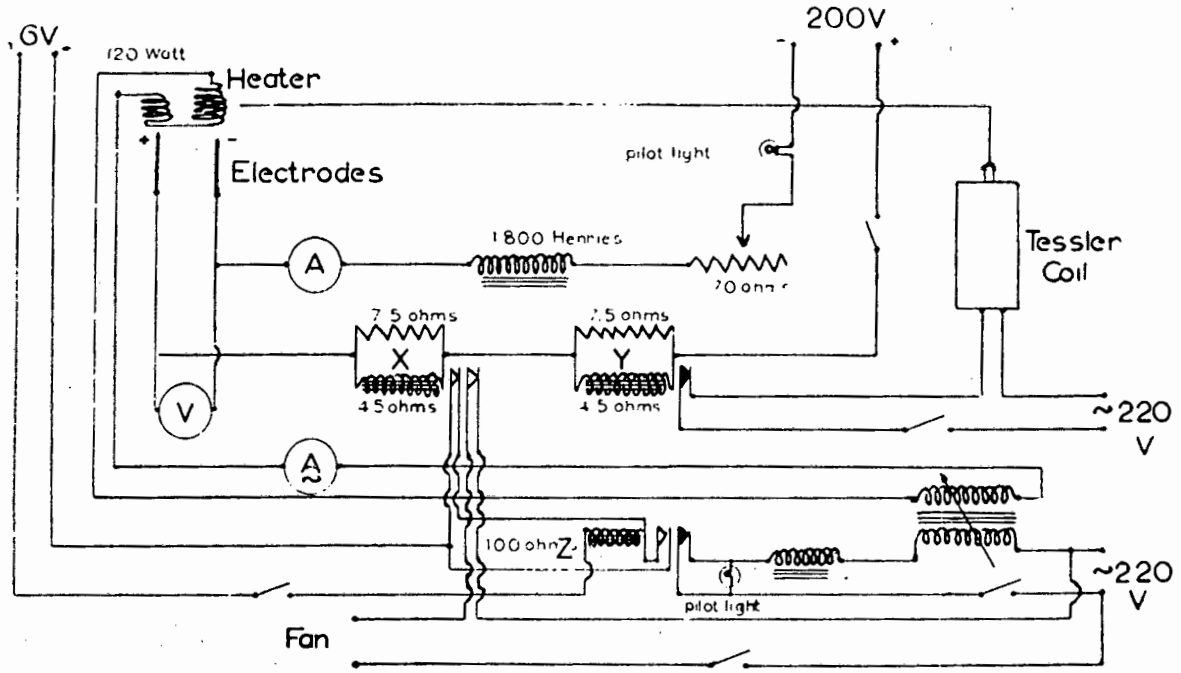
as 8.38 gm./100 c.c. It was possible that the insoluble oxyfluoride might have formed, but this seemed unlikely. The saturated solution still in contact with the solid was treated with 1 gm. of hydrazine dihydrofluoride dissolved in 15 c.c. of water. In all the previous preparations the complex had proved very soluble indeed and it was felt that evidence of solution of the excess would have indicated complex formation. There was, however, no apparent solution of the undissolved indium fluoride. The solution was filtered through Whatman No. 42 filter paper and the undissolved solid weighed. 1.6 gm. had dissolved which is equivalent to 0.2 gm./100 c.c. The clear filtrate was concentrated on the water bath, product was only obtained when all the water had been evaporated. The substance obtained (yield 1.53 gm.) was dried over sulphuric acid and analysed. Found N_2H_4 26.75, In 20.6, F 46%. These figures give a ratio N_2H_4 : In : F :: 4.7 : 1 : 13.5, i.e. the product appeared to be a mixture of indium trifluoride and hydrazine dihydrofluoride, one molecule of the former to five of the latter. The proportions in all probability depended on the amount of indium that had gone into solution.

The undissolved residue on analysis gave N_2H_4O, In 67.5, F 6.6%, which gives a ratio In : F :: 1.7 : 1. As mentioned above formation of the oxyfluoride would have explained the lack of solubility. The oxyfluoride, however, requires a 1:1 ratio; and the above ratio could not be explained.

The preparation was repeated in dilute HF solution. 1.5 gm. of indium trifluoride trihydrate was dissolved in 60 c.c. of 10% HF and



RAMAN LAMP



ELECTRICAL CIRCUITS

Fig 2

0.5 gm. of hydrazine dihydrofluoride. The solution was evaporated on the water bath and product precipitated when the bulk had reduced to 10 c.c. The product was separated, dried and analysed. Found N_2H_4 19.7, In 37.25, F 43%. $(N_2H_6)_2$ $InF_5.2HF$ requires N_2H_4 20.3, In 36.35, F 42.2%.

(4) Unsuccessful attempts to obtain Raman spectra.

Facilities for Raman spectrum investigation were not available. A Hilger D77 constant deviation spectroscope with reasonable dispersion in the range required was available however, and it was decided to try to adapt this instrument for Raman analyses. A special camera suitable for this work was obtained from Hilger and Watts Ltd., and it was felt that this with Kodak Type Oa-O plates (maximum sensitivity in the range required, and best light gathering capabilities for exposures of one minute or longer) might prove adequate.

The conventional light source consists of a number of straight mercury discharge lamps, arranged around the tube containing the specimen being investigated; the whole lamp being surrounded by a diffusing surface to ensure even lighting. These lamps, with their controls, are expensive, and it was felt that the expense in purchasing such a unit was not warranted. A lamp similar to one seen in the chemistry laboratories, University College, London, was constructed instead. The lamp (see Fig. 2) was a length of "Pyrex" tubing bent to a circle, the ends forming mercury reservoirs. The lamp was blown in glass as facilities for working with quartz tubing were not available. This meant that high operating temperatures could not be permitted and

that a large proportion of the ultra-violet light would be filtered out. As the spectrograph used had a glass prism, and as the exciting frequency was that of wave-length 4358 A, this latter disadvantage was of no consequence. Tungsten electrodes were used which after being sealed in position were cleaned by electrolysing N/10 sodium hydroxide in the lamp. This was washed out and the lamp cleaned with aqua regia. It was finally rinsed very thoroughly with distilled water and dried under vacuum.

Trebly distilled (polargraphically pure) mercury was distilled into the lamp at 10^{-3} mm. pressure via a ground glass ball and socket joint which enabled the lamp to be moved in any direction ensuring an even filling of the mercury reservoirs. A spiral was introduced into the filling line between the ball and socket joint and the lamp to slow down the mercury flow.

After the lamp had been filled it was heated under vacuum for 2 hours (to remove adsorbed moisture, gases, etc.) and then a potential of 200 volts was applied and the lamp struck. It was allowed to run for 5 hours under a vacuum of 2×10^{-5} mm. of mercury and then left overnight under vacuum. The following morning the vacuum having held, the lamp was restarted, run for 7 hours and sealed off.

Details of control circuits were not available, and the electrical circuit finally devised is shown on Fig. 2. Basically this consisted of a 200 volt d.c. potential applied to the electrodes. A large inductance was included in this circuit to prevent current fluctuations

breaking the arc; also a variable resistance to alter the current flowing and hence the intensity of the lamp. The lamp was heated primarily by a 120 Watt heating coil wound round the mercury reservoirs. When the lamp struck, relays X and Y operated. Relay Y broke the "Tessler" coil circuit which provided the discharge which started the lamp; should the lamp have gone out for any reason the "Tessler" coil would have started operating automatically. Relay X performed two functions. Firstly it brought a cooling fan into operation, and secondly it operated relay Z. Relay Z in turn broke the heating coil circuit, and also closed an independent 6 volt circuit which ensured that it remained in operation even if relay X opened due to the lamp failing. The heating coils therefore could not be switched on until the 'remake' switch in the heating circuit was opened to interrupt the 6 volt supply. Thus, in the event of a breakdown in the lamp, over-heating and consequential damage to the lamp (not to mention the danger of fire) could not take place. The luminous output was found adequate, and examination of the spectrum showed it to be pure with very little background.

Unfortunately on being run for long periods (Edsall had used exposures of 18 - 24 hours) cracks developed in the tungsten seals. Attempts to obviate this by changing the position of the fan, eliminating the cooling water, altering the connections to the electrodes and modifying the sizes of the resevoirs proved of no avail. The lamp was modified (or remade) five times without a successful exposure resulting.

Subsequent to this, facilities for Raman investigation became available at the N.P.L., Pretoria. A sample of the crystalline hydrazinium pentafluoro-gallate was sent to them for examination. They were unable to get a sufficiently concentrated solution, and were unable to make any successful exposures.

(5) Conductimetric and high frequency titration investigation of the fluorogallates and indates.

(i) Conductimetric titrations.

A modified "Kolrausch" bridge similar to that described by Findlay[73], i.e. point between the measuring arm and the cell earthed, was used. The power supply was a fixed 1000 cycle electronic oscillator with a variable output gain control. The detector consisted of a transformer coupled amplifier which fed through a rectifier into a direct current milliammeter. All the titrations were carried out at constant temperature using lanthanum acetate solution. The lanthanum acetate was prepared as follows: 25 gm. of A.R. lanthanum chloride was dissolved in 40 c.c. of water. Ammonia gas was bubbled through the solution and the hydroxide precipitated. The hydroxide was dissolved in 40 c.c. A.R. glacial acetic acid. The solution was concentrated to approximately 40 c.c. and allowed to stand. After 48 hours a crop of crystals was obtained (5.9 gm.). The mother liquor and washings were evaporated almost to dryness and another 46 gm. of product resulted. The lanthanum acetate was analysed and a standard solution made by dissolving 8 gm. in 1 litre of water. The solution was standardised using A.R.sodium fluoride. 1 c.c. $\equiv$ 0.001065 gm. F^-.

(a) Hydrazinium dihydrofluoride. 2.5×10^{-3} M.

c.c. lanthanum acetate	$1/R \times 10^{-4}$ mhos
0	9.10
1	7.25
2	6.52
3	10.42
4	13.93

(b) Gallium trifluoride trihydrate. 2.5×10^{-3} M.

c.c. lanthanum acetate	$1/R \times 10^{-4}$ mhos
0	2.90
1	3.55
2	4.30
3	6.00
4	8.20
5	10.60
6	13.30
7	15.29
8	17.50
9	19.90
10	21.80

(c) Hydrazinium hexafluorogallate. ($N_2H_6GaF_4 2HF$) 2.5×10^{-3} M.

c.c. lanthanum acetate	$1/R \times 10^{-4}$ mhos
0	10.10
1	9.69
2	9.28
3	9.33
4	9.61
5	9.80
6	10.40
7	12.26
8	14.15
9	16.40

(ii) Molar conductances.

The same apparatus as was used for the conductimetric titrations was used, the cell constant being determined using Molar

potassium chloride.

$$\lambda = \frac{1000\ K}{C}$$, where K = cell constant, C = concentration.

(a) Gallium trifluoride trihydrate.

$\sqrt{C}$ M x 10^{-2}	λ ohm^{-1} cm.^{2}
1.100	251
1.575	223
2.250	182(.5)
3.210	127(.5)

(b) Hydrazinium hexafluorogallate ($N_2H_6GaF_4.2HF$)

$\sqrt{C}$ M x 10^{-2}	λ ohm^{-1} cm.^{2}
0.40(0)	1000
0.62(5)	540
0.85(0)	280
1.25(0)	220
1.80(0)	175
2.50(0)	150
5.00(0)	100
7.10(0)	80

(iii) High frequency titrations

A high frequency titrimeter as described by Dowdall, Sinkinson and Stretch[65] was constructed and the titrations were carried out as described by them, namely using lanthanum acetate, the solution titrated being buffered with acetic acid. The same solution was used as for the conductimetric titrations, but was restandardised. 1 c.c. ≡ 0.001215 gm. F^-. The actual numerical values are meaningless as the initial setting was arbitrarily chosen.

(a) Gallium trifluoride trihydrate. 2.2×10^{-3} M.

c.c. lanthanum acetate	μA
0	36.5
0.1	35.5
0.2	34.5
0.3	33.5
0.4	32.5
0.5	31.7
0.6	31.2
0.7	31.0
0.8	31.0
0.9	31.0
1.0	31.5
1.1	32.0
1.2	32.7
1.3	33.4
1.4	34.0
1.5	34.8

(b) Gallium trifluoride trihydrate. 4.4×10^{-3} M.

c.c. lanthanum acetate	μA
0	31.0
0.1	31.0
0.2	31.0
0.3	31.0
0.4	31.0
0.5	31.0
0.6	31.0
0.7	31.0
0.8	31.0
0.9	31.0
1.0	31.3
1.1	31.8
1.2	32.3
1.3	32.7
1.4	33.0
1.5	33.8

(c) Hydrazinium hexafluorogallate ($N_2H_5GaF_4 2HF$) 2.5×10^{-3} M.

c.c. lanthanum added	μA
0	34.0
0.5	29.4
1.0	25.6
1.5	22.0
2.0	21.0
2.5	21.0
3.0	21.0
3.5	22.0
4.0	24.0

(d) Hydrazinium heptafluoroindate $(N_2H_5)_2InF_5 2HF$. 2.5×10^{-3} M.

On solution:

c.c. lanthanum added	μA
0	36.0
0.5	35.0
1.0	34.0
1.5	33.0
2.0	32.0
2.5	31.0
3.0	30.0
3.5	29.0
4.0	28.2
4.5	28.2
5.0	28.2
5.5	29.0
6.0	30.0
6.5	31.0
7.0	32.0

After standing for 3 weeks:

c.c. lanthanum added	μA
0	39.1
0.5	37.6
1.0	36.0
1.5	34.6
2.0	34.0
2.5	32.6
3.0	32.0
3.5	31.0
4.0	30.0
4.5	30.0
5.0	30.0
5.5	31.8

6.0	33.0
6.5	34.0
7.0	36.0
7.5	39.8
8.0	46.0

(e) Hydrazinium fluorogallate with 14 extra HF molecules $(N_2H_5)_2GaF_5.14HF$. 2.5×10^{-3} M.

On solution:

c.c. lanthanum added	μA
0	41.0
0.5	38.4
1.0	34.8
1.5	32.0
2.0	29.0
2.5	26.0
3.0	24.0
3.5	26.0
4.0	30.0
4.5	37.0
5.0	44.0

After standing for 3 weeks:

c.c. lanthanum added	μA
0	31.0
1.0	26.0
2.0	21.4
3.0	18.0
4.0	28.0
5.0	38.5

(6) Thermal decomposition of the fluorogallate.

The compounds $(N_2H_5)_2GaF_5.HF$ and $(N_2H_5)_2GaF_5.14HF$ were investigated by heating in an open platinum dish in an oven, the dish and contents being weighed hourly. No change in weight for five successive weighings was considered sufficient to assume constant weight.

Further experiments were done on the compound with fourteen extra molecules of HF. The compound was heated at constant temperature and the rate of loss of weight was observed. This was done both with the compound heated in an open platinum dish in an oven at atmospheric pressure, and with the compound in a polythene boat in a drying pistol at 40 m.m. of mercury. During this latter experiment the boat became discoloured due to polymerisation. The effect of heating this tubing was investigated, no significant change in weight was noted, however.

Different samples were taken, and the tables below are the results of a number of experiments. Generally constant weight was reached after 6 - 8 hours.

(i) $(N_2H_5)_2GaF_5.HF$ heated at 760 m.m.

°C	% Loss	
60	0.3	
106	2.3	
116	3.0	(another sample gave 1.7)
130	6.7	
139	9.4	
150	13.2	
164	44.6	(after 27 hours heating)
224	50.2	(after 24 hours heating)
282	50.3	(after 25 hours heating)

(ii) $(N_2H_5)_2GaF_5.14HF$ heated at 760 m.m.

°C	% Loss
65	1.13
84	6.84
104	11.83
115	13.28
120	18.00
125	23.7
131	27.75
154	31.95
183	33.7
205	44.9
238	51.3
290	59.5

(iii) (a) $(N_2H_5)_2GaF_5.14HF$ heated at 80°C, 760 m.m.

Time	% Loss
0	0
2.5	1.85
3.5	2.28
5	3.15
6	3.15
7.5	3.80
8.5	4.34
9.5	5.11
10.5	5.11
11.5	5.42
13	6.50
14	7.50
15	7.50
16	7.50
18.5	9.23
19.5	9.65
20.5	10.42
21.5	10.75
23	10.75
24	10.75
25	10.75
26	11.34
27	11.84
28	11.84
29	12.05
30	12.05
31	12.05
33	12.05
34.5	12.05
36.5	12.05
39	12.05
41	12.05
44	12.05

(b) $(N_2H_5)_2GaF_5.14HF$ heated at 135°C and 760 m.m. starting with compound which had lost 12.05%.

Time	% Loss
1	16.4
2	20.3
2.5	21.6
3	21.6
3.5	22.8
4	24.8
4.5	25.1
5	25.95
5.5	26.15
6	27.1
6.5	27.1
7	28.3
7.5	29.3
8	29.3
8.5	29.3
9	30.3
9.5	30.4
10	30.5
10.5	31.4
11	31.4
11.5	31.8
12.5	32.65
13	33.5
14	33.5
15	33.5
17	33.8
18	34.7
20	34.7
22	34.7

(c) $(N_2H_6)_2GaF.14HF$ heated at 238°C and 760 m.m. starting with compound which had lost 34.7%.

Time	% Loss
0	34.7
0.5	37.7
1.5	39.0
2	40.8
3.25	42.0
4	44.2
5	44.4
5.5	45.3
6.5	47.3
7.5	48.8
8.5	49.4
9.5	50.8
10.5	51.8
11.5	53.1
12.5	54.2
13.5	55.4

(iv) $(N_2H_6)_2GaF_5.14HF$ heated at 80°C and 40 m.m.

Time	% Loss	Time	% Loss
1	2.86	31	26.0
2	4.63	32	26.0
4.5	8.16	33	27.8
5.5	8.50	34	27.8
7	10.14	35.5	27.8
8	10.14	37	28.2
9	12.11	38	28.55
10	12.9	39	28.55
11	14.95	41	28.55
12	14.95	42	29.1
13	14.95	44	29.1
14	17.42	45	29.4
15	19.55	47	31.3
17	20.4	48	31.3
19.5	21.55	50	32.0
20.5	21.55	51	32.2
21.5	22.9	52	32.2
22.5	23.4	52.5	32.2
24	23.4	54.5	32.2
25	23.95	56	32.6
26	24.3	58	33.4
27	24.3	60	33.5
28	24.65	61	33.5
29	25.4	63	34
30	25.4	64	34.5

Time	% Loss	Time	% Loss
66	34.8	75	37.0
67	35.1	78	38.6
69	35.6	81	38.2 (?)
71	36.5	84	38.4
73	37.3 (?)	87	39.2
		89	39.5

Samples were taken at various stages during the heating, analysed and the hydrazine:gallium ratio calculated.

Under 12% loss in weight the ratio was approximately 2:1, from this point hydrazine began to be lost as well, and the ratio had become approximately 1:1 by the time the 34% loss had been recorded. Thereafter the second hydrazine began to be lost as well, and the ratio became x:1 where x became less than one and decreased rapidly.

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